VERSION 1.0 _REVISION DATE 22/10/2021

TECHNICAL DATA SHEET

Roboze PEEK

Overview

Polyetheretherketone (PEEK) is a semi-crystalline, high-performance engineering thermoplastic. It belongs to polyketone family of polymers (PEK, PEEK, PEEKK, PEKK, PEKEKK) and amongst them, it is the most widely used and manufactured in large scale.

PEEK offers a unique combination of mechanical properties such as resistance to chemicals, wear, fatigue and creep, as well as exceptionally high-temperature resistance. It also has good resistance to combustion and good electrical performance.

The high thermal stability is provided by the diphenylene ketone groups, which impart high strength and high resistance to oxidation. Flexibility in the polymer backbone is provided by ether linkages. Due to the semi-crystalline nature of this polymer, its low tendency to creep, and its good sliding and wear, properties are retained over a wide temperature range.

PEEK is known for its excellent chemical resistance to many organic and inorganic chemicals and for its exceptionally good resistance to hydrolysis in hot water. For this reason, the polymer is often subjected to autoclave processes.

Applications

PEEK finds application in a wide range of industrial sectors.
Because of its good wear resistance, mechanical properties, and machinability, mechanical parts can be made of PEEK to replace steel in some applications.

Examples are high-speed rotors, intricate bearing shells, aircraft landing gear hubcaps, and aerospace P-clamps. Polyetherketones are usually not attacked by prolonged exposure to (sea) water or steam, which makes them ideal candidates for use in applications such as medical devices, subsea equipment and valve components.

Design phase

The preparation of the samples and the execution of the individual tests followed the guidelines imposed by the associated regulations. Analyses on the relevant samples were carried out by an accredited, independent and impartial third party laboratory.[1]

---

[1] Although data measured in a controlled environment can provide an indication of the chemical/physical and mechanical properties of the material and thus enable comparison between different materials, the results of these tests may not be the same as those observed in the final component.

This phenomenon may be caused by the presence of geometric features or manufacturing conditions that may contribute to modifying the material behaviour. Furthermore, the properties of polymeric materials are a function of both temperature and environmental factors (solar radiation, humidity, etc.), which is why the effect of these variables should also be considered during the design phase, both in the case of short-term and long-term exposure.

In view of the above, it is recommended that a prototype be made in advance during the design phase to empirically verify its properties in the operating conditions required by the specific application.

VERSION 1.0 _REVISION DATE 22/10/2021

TECHNICAL DATA SHEET

Roboze PEEK

Manufacturing Process

Specimens were manufactured on a Roboze ARGO 500 fed with a filament with a diameter of 1.75 ± 0.05 mm. This thermoplastic filament was subsequently extruded through a 0.6 mm diameter nozzle. To minimize the concentration of water molecules adsorbed and absorbed by the filament due to exposure to the atmospheric environment, before starting the printing process, PEEK spools were subjected to a drying cycle at a temperature of 100°C for 12 hours in HT Dryer.

The temperature of the working chamber was set to 160°C. To allow isothermal conditions within the hot chamber, a 2 hour delay took place before starting the printing process.

Printing conditions for following data tables were:

- Chamber Temperature = 160°C
- Extrusion Temperature = 470°C
- Printing speed = 1200 mm/min
- Layer height = 0,2 mm
- Infill percentage= 100%
- 2 Shells

At the end of the printing process the samples are subjected to the phase of manual removal of the support structures.

The additive manufacturing technology produces intrinsically anisotropic components. As the orientation of the component on the printing plate changes, it will be possible to observe variations in terms of both the properties of the final article and the productivity of the printing process. Keeping in mind what has been written above, it is possible to identify three different orientations on the building plate that are named as follows:

- Flat (or XY)
- On Edge (or XZ)
- Upright (or ZX)

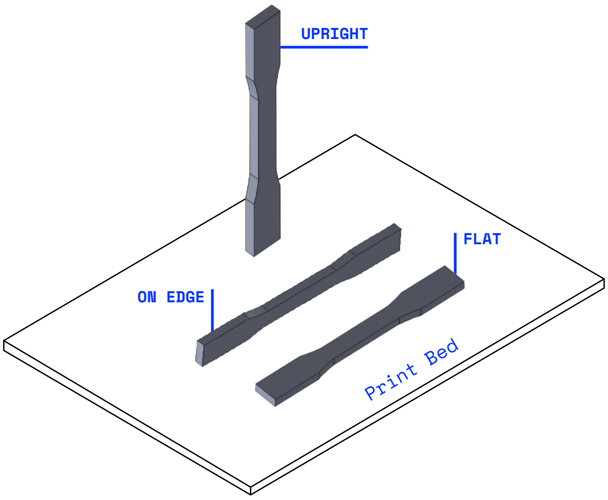

Figure 1 Example of On Edge, Upright and Flat orientation on the building plate

TECHNICAL DATA SHEET

Roboze PEEK

PEEK properties Summary

MECHANICAL PROPERTIES

PROPERTY	OPERATING CONDITIONS	UNITS	ORIENTATION				TEST METHOD
			XZ	XY 0°	XY 45°	ZX	
Tensile Strength	25°C	MPa	95	89,9	87,4	53,0	ASTM D638
Young Modulus	25°C	GPa	3,5	3,5	3,4	3,3	ASTM D638
Elongation at Tensile Strength	25°C	%	4,8	4,7	4,5	1,9	ASTM D638
Tensile Strength	80°C	MPa			66,5		ASTM D638
Young Modulus	80°C	GPa			3,4		ASTM D638
Elongation at Tensile Strength	80°C	%			3,2		ASTM D638
Tensile Strength	120°C	MPa			56,9		ASTM D638
Young Modulus	120°C	GPa			3,3		ASTM D638
Elongation at Tensile Strength	120°C	%			3,0		ASTM D638
Tensile Strength	200°C	MPa			37,2	20,5	ASTM D638
Young Modulus	200°C	GPa			0,5	0,3	ASTM D638
Elongation at Tensile Strength	200°C	%			185	70	ASTM D638
Flexural strength	25°C	MPa			116,0		ASTM D790
Flexural modulus	25°C	GPa			2,8		ASTM D790
Compressive strength @ ε=1%	25°C	MPa				111,8	ASTM D695
Compressive strength @ ε=20%	25°C	MPa				135,0	ASTM D695
Compressive Modulus	25°C	GPa				4,0	ASTM D695
Shore Hardness	D scale				83,7		ASTM D2240
Coefficient of Friction	10 N				0,25		Pin on Disk

TECHNICAL DATA SHEET

Roboze PEEK

PEEK properties Summary

PHYISICAL PROPERTIES

PROPERTY	OPERATING CONDITIONS	UNITS	ORIENTATION				TEST METHOD
			XZ	XY 0°	XY 45°	ZX	
Melting Temperature		°C	338				DSC
Glass transition temperature		°C	146				DSC
Heat Deflection Temperature	1.82 MPa	°C			161		DMTA
Coefficient of Thermal Expansion	20°C - 50°C	10^{-6} K^{-1}	46				ASTM E228
Coefficient of Thermal Expansion	20°C - 100°C	10^{-6} K^{-1}	48				ASTM E228
Coefficient of Thermal Expansion	20°C - 140°C	10^{-6} K^{-1}	52				ASTM E228
Coefficient of Thermal Expansion	150°C - 200°C	10^{-6} K^{-1}	127				ASTM E228
Thermal conductivity*	25°C	W/m-K			0,25		
Thermal conductivity	250°C	W/m-K			0,42		
T_5%	Air	°C	569				TGA
T_5%	N2	°C	569				TGA
Glow Wire Test – GWFI *	2mm thickness	°C	960				IEC 60695-2-12
Service Temperature*	During lifetime max 200h	°C	260°C				
Insulation Resistance Strip Electrode *	R25	Ω	$>10^{12}$				DIN IEC 60127 A
Surface Resistance *	ROB	Ω	$>10^{12}$				DIN IEC 60093
Dielectric Constant *	23°C 1 kHz		3,1				IEC 60250
Dielectric Constant *	23°C 50 Hz		3				IEC 60250

GENERAL

PROPERTY	OPERATING CONDITIONS	UNITS	VALUE	TEST METHOD
Specific gravity		g/cm^3	1,31	ISO 1183-3
Water Absorption	23°C/24h	%	<0.1	ISO 62
Melt Volume Rate		cm^3/10min	22	ISO 1133
Melt Viscosity	400°C	Pa • s	350	ISO 11443
Color			Beige	

* The information may come from the raw material, the semi-finished product or an estimate. Specific individual tests are recommended according to the application conditions required for the final implementation..

TECHNICAL DATA SHEET

Roboze PEEK

Mechanical Properties

Tensile Properties

The tensile test is a destructive test useful to characterize the properties of materials when subjected to uniaxial tensile loads. A specimen of standard dimensions, having a "dogbone" geometry, is clamped by means of appropriate clamps to two crossbeams.
The movable crossbeam can move upwards, thus bringing the specimen into a tensile state. Once the displacement speed of the crossbar has been set, the load applied and the deformation undergone by the sample are monitored during the test.
In output the system is able to provide a Cartesian graph where on the ordinates is represented the stress (σ), i.e. the ratio between the force applied to move the mobile crosshead at constant speed and the minimum section of the test specimen "dogbone", while on the abscissae is reported the strain (ε)i.e. the percentage ratio between the variation of length of the test specimen with respect to its initial dimensions ($\Delta\ell$) and its nominal length before the start of the test (ℓ_0).

The stress-strain curve will be a function of the nature of the material. The characteristic parameters that can be derived from this curve are: tensile strength (σ_M), Young's modulus (E) and strain at break (ε_B).

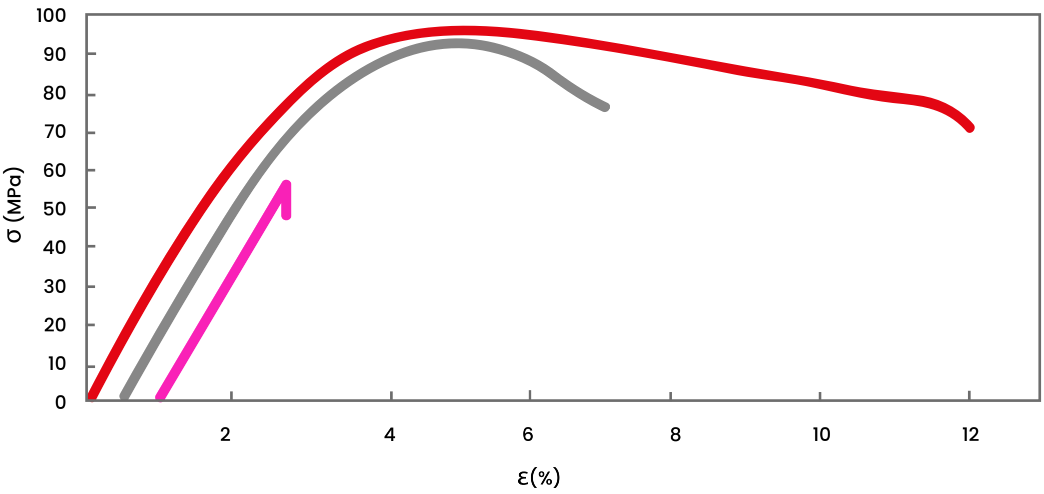

Figure 2 Comparison between tensile test behavior of PEEK samples built in different orientations

The initial section of the curve shows a region of linear elastic deformation. In this region (also called the Hookean region of the material), the material undergoes an instantaneous and reversible strain linearly dependent on the applied stress.

The angular coefficient of the tangent line to the linear elastic region is defined as Young's Modulus, which is the constant of proportionality between the strain undergone by the material and the applied stress. Young's modulus is generally measured from the stresses at 0.05% and 0.25% strain.

TECHNICAL DATA SHEET

Roboze PEEK

Components manufactured by additive manufacturing have anisotropic mechanical properties. Since the aim of the additive manufacturing process is often to create parts of arbitrarily complex geometry, it is very difficult to align the sample in the direction that maximizes its mechanical properties.

Variations in spatial orientation lead not only to a change in the mechanical strength values of the component, but also affect the fracture mechanism: In the case of samples in XZ orientation, the specimen exhibits greater toughness, showing the phenomenon of necking before the fracture. In the case of specimens printed in ZX orientation, the fracture behavior is typical of a brittle material, since the fracture occurs along the linear elastic stretch of the σ-ε curve.

The standard followed to perform the characterization of the samples was ASTM D638. A speed of 1 mm/min was used to calculate the tensile modulus, thereafter, the speed was increased up to 50 mm/min until the specimen failed. It should be remembered that the results of the tensile test are a function of the set test speed, which is why for a proper comparison between different materials it is important to know in advance the speed at which the test was performed.

Table 1 Tensile properties of PEEK measured at 25°C for different specimen orientations

TENSILE TEST ASTM D638		ORIENTATION			
	UNIT OF MEASURE	XZ	XY 0°	XY ±45°	ZX
Tensile Strength	MPa	95	89,9	87,4	53,0
Elongation at Tensile Strength	%	4,8	4,7	4,5	1,9
Young Modulus	GPa	3,4	3,5	3,4	3,3

Stress-Strain behavior at different temperature

Thermoplastic polymers, by their nature, undergo a progressive reduction of their viscosity with increasing temperature. This leads to a progressive softening of the material until it reaches complete melting.

Obviously, as it is possible to guess, the mechanical properties of the final product will depend on the working temperature: the higher the temperature, the lower the performance of the material. However, semi-crystalline thermoplastic polymers such as PEEK, thanks to the presence of crystalline domains, can maintain high mechanical properties even at temperatures above the glass transition temperature.

The variation of the mechanical properties as a function of temperature can be analyzed by performing tensile tests in a heated chamber at the desired temperature.

TECHNICAL DATA SHEET

Roboze PEEK

Table 2 Tensile properties of PEEK measured at 80°C for XY ± 45° specimens

TENSILE TEST ASTM D638			
TEMPERATURE		UNIT OF MEASURE	XY ±45°
80°C	Tensile Strength	MPa	66,5
	Young Modulus	GPa	3,4
	Elongation at Tensile Strength	%	3,0

Table 3 Tensile properties of PEEK measured at 120°C for XY ± 45° specimens

TENSILE TEST ASTM D638			
TEMPERATURE		UNIT OF MEASURE	XY ±45°
120°C	Tensile Strength	MPa	56,9
	Young Modulus	GPa	3,3
	Elongation at Tensile Strength	%	3,0

Table 4 Tensile properties of PEEK measured at 200°C for XY ± 45° specimens

TENSILE TEST ASTM D638			
TEMPERATURE		UNIT OF MEASURE	XY ±45°
200°C	Tensile Strength	MPa	37,2
	Young Modulus	GPa	0,5
	Elongation at Tensile Strength	%	185

The variation of tensile strength as a function of temperature for XY ±45° specimens is plotted below.

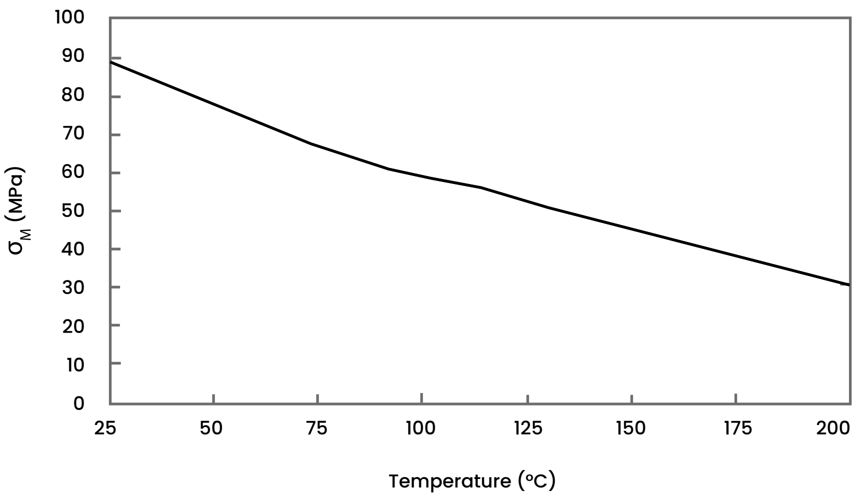

Figure 3 Variation of tensile strength as a function of temperature from 25°C to 200°C

TECHNICAL DATA SHEET

Roboze PEEK

Flexural Properties

During the design phase, the knowledge of the bending behavior of a material, results to be an essential key parameter for the correct structural dimensioning of the component.

Assuming to consider a bar of material supported at two points at the end and loaded with a load in a direction perpendicular to the center, it is possible to demonstrate how the stresses originating inside the body present an axial stress distribution of linear type: the stress σ reaches maximum values in modulus and opposite in sign at the extremes of the section and is zero at the neutral axis.

Reason for which the points below the neutral axis (and therefore the surface on which the applied load insists) will be in a state of compression, while the points above the neutral axis (and therefore belonging to the surface free from the action of the load) will present a state of traction.

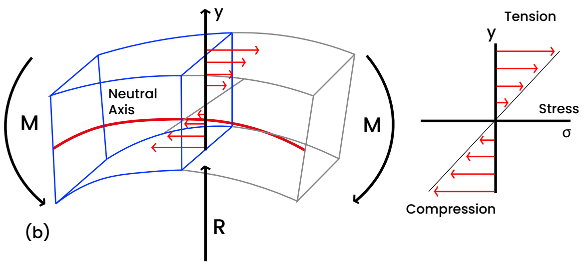

Figure 4 Stress variation along cross section of a beam subjected to flexural loads

The flexural behavior of PEEK was evaluated according to ASTM D790. The samples are bars with dimensions 12.7mm x 127mm x 3.2mm.

The testing speed was set to 1.35 mm/min and the support span was 50.8 mm.
The strength is determined by the stress at break while the modulus is calculated by the tangent method.

Table 5 PEEK Flexural Properties

ORIENTATION	E_F (MPa)	σ_F(MPa)
XY ±45°	2,8	116,0

Compression Properties

Compressive stresses are inherently present in many engineering systems either due to the application of a compressive load directly on the component or due to the application of impact or bending loads. Another phenomenon directly related to compressive loads is buckling, which severely limits the efficiency of systems leading to an underutilization of the real properties of the material.

TECHNICAL DATA SHEET

Roboze PEEK

The reference standard used for the determination of the compression properties of PEEK was ASTM D695. The specimens used are square-based prisms with different heights depending on whether you want to measure: the modulus or the stress.

The characteristic dimensions of the specimens are as follows:

- Compressive strength: (b) 12.7mm x (h) 12.7mm x (ℓ) 25.4mm
- Modulus of Compression: (b) 12.7mm x (h) 12.7mm x (ℓ) 50.8mm

For both tests, a testing speed of 13 mm/min was set.

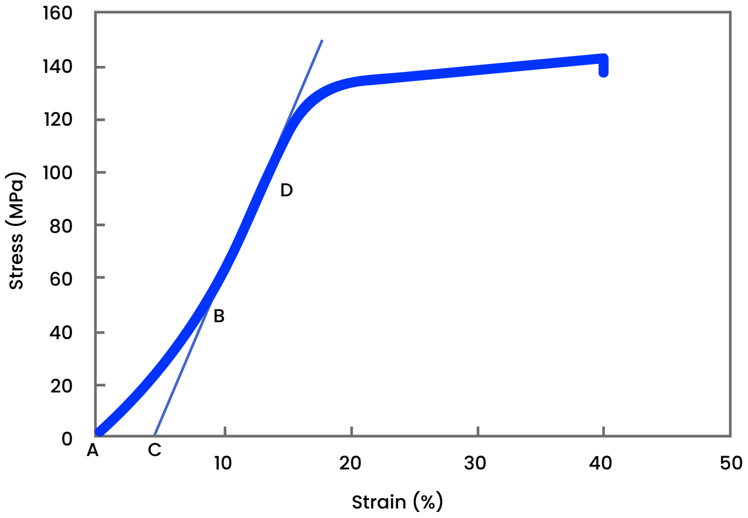

Figure 5 Stress strain curve for a PEEK sample subjected to compression test

Except for the initial toe region AC (typical measurement artifact not representing a property of the material), PEEK shows Hookeian (linear) behavior. The point of intersection (C) between the x-axis and the extension of the linear section (BD) is the corrected point of origin on the x-axis from which all strain were measured.

Table 6 Compressive strength and modulus values of PEEK at 25°C

E_C	σ_C @ε=1%	σ_C @ε=20%
4,0	111,8	135,0

The data reported in the table represent the average value of the values measured on samples placed in 15 different spatial coordinates inside the working chamber[2].

---

[2] See https://bit.ly/2ZFVM9v for more details about the operating procedure.

TECHNICAL DATA SHEET

Roboze PEEK

Hardness Test

The hardness is a numerical value that indicates the characteristics of plastic deformability of a material and allow to determine the resistance offered by a material to be penetrated by another (penetrator). The test of hardness used to characterize the behavior of PEEK is the ASTM D2240 Shore D test method. In this test, the specimen is first placed on a hard flat surface. Then the indenter is pressed into the specimen making sure that it is parallel to the surface and finally the hardness is read within a certain amount of time of firm contact with the specimen.

Table 7 Shore D Hardness values of PEEK

SHORE D HARDNESS	ASTM D2240	83,7

Coefficient of friction

The debris that originates from the wear process generates a film at the interface between the surface of the sample under examination and the counterpart, which allows to reduce the friction coefficient and facilitate the sliding. Study on tribological properties of PEEK were performed on a pin-on-disc tribometer. The methodology of the test consists in fixing the PEEK disc on a rotating plate and the steel pin (counterpart) is pushed against the disc with 10 N load. The pin stays on the disc with two degrees of freedom: one vertical, which allows its direct contact with the surface of the disc, and the other horizontal, which is responsible for the friction contact. The counterpart is a 100Cr6 steel sphere with a diameter of 6 mm. Before each test, the sphere was washed with acetone to remove any residue and contamination. The test conditions were as follows:

- Applied load: 10 N
- Track radius: 15 mm
- Sliding speed: 20 cm/s
- Sliding distance: 1000 m

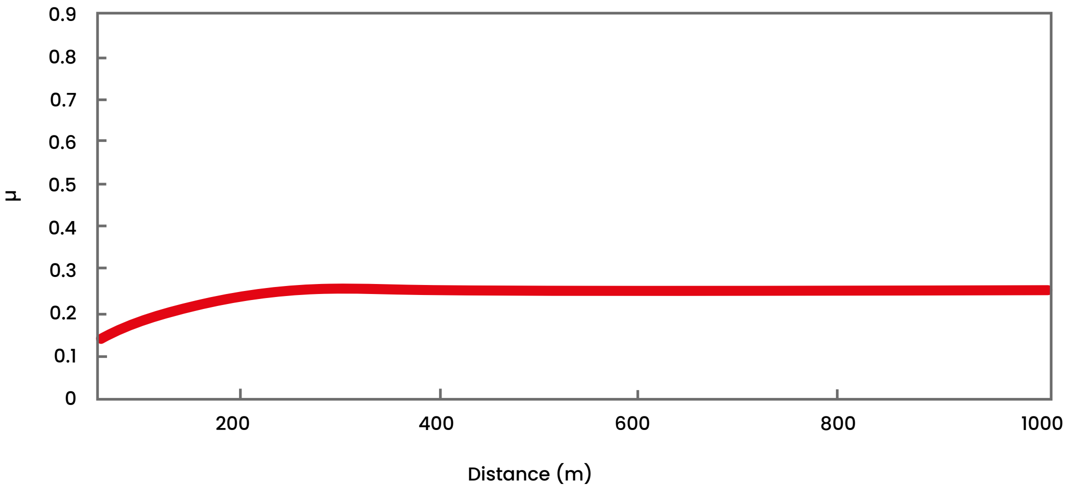

Figure 6 Variation in coefficient of friction as a function of sliding distance

The evolution of the friction coefficient can be observed. Initially, an increase in friction coefficient associated with the initial running-in period was observed then it stabilizes around values of 0,25.

TECHNICAL DATA SHEET

Roboze PEEK

Table 8 Synthesis of experimental data for pin on disc test

PIN ON DISC TEST CONDITION	VALUE
• Applied load: 10 N • Track radius: 15 mm • Speed: 20 cm/s • Distance: 500 m • Pin : Steel 100Cr6	0,24

Chemical Compatibility

PEEK is known for its excellent chemical resistance to many organic and inorganic chemicals and for its exceptionally good resistance to hydrolysis in hot water. The aryl rings in PEEK are linked via ketone and ether groups in "para" position (i.e. placed at opposite ends of the ring).

The resonance-stabilized chemical structure of PEEK results in delocalization of higher orbital electrons along the entire macromolecule, making it exceptionally unreactive and intrinsically resistant to chemical degradation.

CHART CODES
R - Resistant
LR - Limited Resistance
NR - Not Recommended
ND - No Data

CHEMICAL	RESISTANCE		
	20°C/68°F	60°C/140°F	100°C/212°F
Acetaldehyde	NR	NR	R
Acetone	R	R	R
Acetylene	R	R	R
Acid fumes	R	R	R
Alcohols	R	R	R
Aliphatic esters	R	R	R
Ammonia, aqueous	R	R	R
Aromatic solvents	R	R	R
Benzene	R	R	R
Carbonic acid	R	R	R
Caustic soda & potash	R	R	R
Chlorobenzene	R	R	R

TECHNICAL DATA SHEET

Roboze PEEK

Copper salts (most)	R	R	R
Cyclohexane	R	R	R
Detergents, synthetic	R	R	R
Ether	R	R	R
Fatty acids (>C6)	R	R	R
Ferric chloride	R	R	R
Formaldehyde (40%)	R	R	R
Glycol, ethylene	R	R	R
Hydrochloric acid (10%)	R	R	R
Hydrochloric acid (conc.)	R	R	ND
Hydrocyanic acid	R	R	R
Hydrogen peroxide (30%)	R	R	R
Hydrogen peroxide (30 - 90%)	R	R	ND
Hydrogen sulphide	R	R	R
Hypochlorites (Na 12-14%)	NR	NR	NR
Lactic acid (90%)	R	R	R
Mercury	R	R	R
Methanol	R	R	R
Milk products	R	R	R
Moist air	R	R	R
Napthalene	R	R	R
Nickel salts	R	R	R
Nitric acid (<25%)	R	R	R
Nitric acid (50%)	R	R	R
Nitric acid (90%)	NR	NR	NR
Nitric acid (fuming)	NR	NR	NR
Oils, diesel	R	R	R
Oils, essential	R	R	R
Oils, mineral	R	R	R
Oils, vegetable and animal	R	R	R
Ozone	R	R	R
Phosphoric acid (20%)	R	R	R
Phosphoric acid (50%)	R	R	R
Phosphoric acid (95%)	R	R	R
Sea water	R	R	R
Silicone fluids	R	R	R
Silver nitrate	R	R	R
Sodium carbonate	R	R	R
Sulphates (Na, K, Mg, Ca)	R	R	R
Sulphites	R	R	R
Sulphuric acid (<50%)	R	ND	ND
Sulphuric acid (70%)	R	R	R
Sulphuric acid (95%)	NR	NR	NR
Urea (30%)	R	R	R
Water, distilled	R	R	R
Water, soft	R	R	R
Water, hard	R	R	R

TECHNICAL DATA SHEET

Roboze PEEK

Thermal Properties

Glass Transition and melting temperature

Unlike thermosetting polymers, when heated, thermoplastic polymers undergo a progressive softening process until they reach complete melting. The energy supplied through heat irradiation can weaken and progressively break the Van der Walls bonds between the various polymer chains.

This phenomenon involves a reduction in the stiffness of the polymer, which ends behaving as an elastic solid and begins to assume the typical behavior of a viscoelastic material.

The higher the temperature, the greater the viscous component will be compared to the elastic one. Glass transition temperature (T_g) is described as the temperature at which 30-50 carbon chains of the amorphous region start to move. As the temperature rises, the energy supplied to the system increases, allowing the progressive dissolution of the crystalline domains. The temperature at which this phenomenon occurs is called melting temperature (T_m).

The technique that allows to determine the T_g and the T_m is the Differential scanning calorimetry (DSC).

DSC analyses were performed according to the following cycle: heating up from 80 to 400°C at 10°C/min, 3 min isothermal step at 400 C, cooling down to 80 C at 10 °C/min, 5 min isothermal step at 80 °C, final heating up from 80 to 400°C at 10 °C/min. Test was performed in nitrogen atmosphere.

The figure shows the DSC spectrum of the PEEK filament used for printing the samples. From the diagram it is possible to analyze the behavior of the material during the first heating cycle, the subsequent temperature-controlled cooling step and finally the second heating cycle (red, black, and green curve respectively). Such a temperature scan provides different information about the sample.

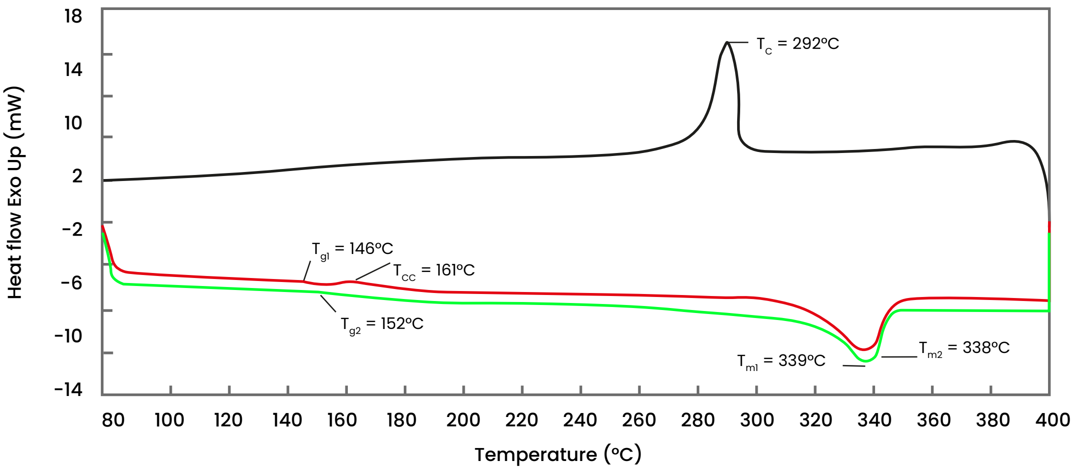

Figure 7 DSC spectrum of the sample representing the three thermal cycles

TECHNICAL DATA SHEET

Roboze PEEK

Info about coefficient of thermal expansivity provides quantitative characterization of expansion properties, which is an important designing index of the composite structure. The smaller α_T gives an advantage of stability during the printing phase or using process in high temperature environments.

Materials shows temperature dependence in their coefficient of thermal expansivity, especially above T_g. Therefore, a single reported number for CLTE will not accurately reflect the expansion behavior, except below T_g where α changes little. Nonetheless, it is customary to select a representative value of CLTE for comparison purposes.

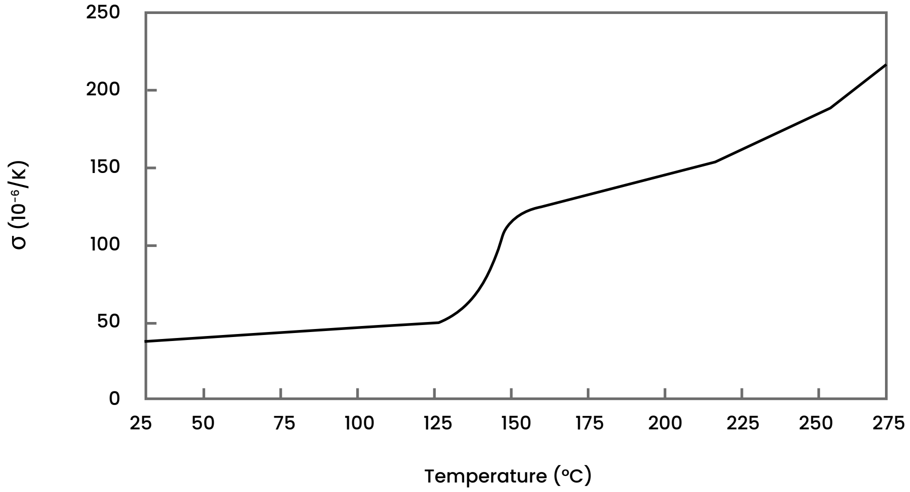

Figure 8 Variation of the linear thermal expansion coefficient with temperature

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed in a double cantilever configuration. A temperature range of 25 to 300°C, a heating rate of 3°C/min, a frequency of 1 Hz and 0.05% oscillation amplitude were set (the test was performed in strain controlled mode). DMTA measurements are used to assess the polymer stiffness and mobility of macromolecules under dynamic conditions. The dynamic mechanical behavior of PEEK samples has been studied and the following figure shows the variation of the storage (E') and loss (E") moduli with temperature.

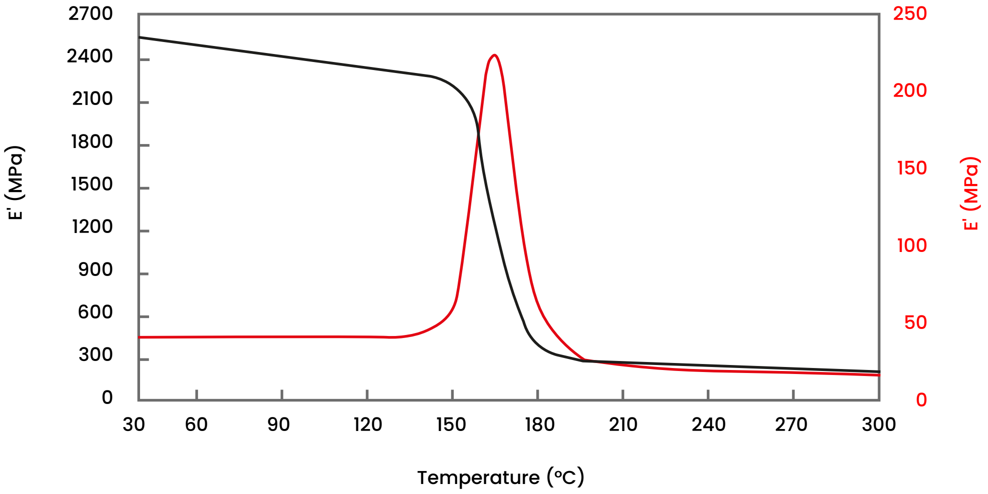

Figure 9 Development of storage (E') and loss module (E'') as a function of temperature

Roboze PEEK

In the temperature range of 30-130°C, the material has a relatively high storage modulus and a low loss modulus. This results from the fact that in this temperature range the chains are locked in a rigid network.

In the range 130-200°C, there is a marked drop in the storage modulus, which is accompanied by a peak in the loss modulus; in this region the polymer chains acquire greater mobility, and the polymer undergoes a progressive phase transition from the condition of a rigid glassy material to that of a viscous fluid. Finally, in the range 200-300°C, a rubbery plateau can be observed in which both moduli remain constant. Here, the translational movements occurring in the liquid state are limited by the entanglements of the macromolecules acting as temporary crosslinks.

The Heat Deflection Temperature (HDT) was extrapolated from the storage module graph. The HDT at 1.82 MPa was determined as the temperature at which the storage module reaches 800 MPa in DMTA testing.

Table 10 Deflection Temperature

DEFLECTION TEMPERATURE AT 1.8 MPa	DMTA	°C	161

Thermal conductivity

Among the main thermophysical parameters to characterize the heat transfer properties of a material we find Thermal Conductivity.

To determine thermal conductivity, it is important to record thermal diffusivity and specific heat capacity. Thermal diffusivity was measured by laser flash method. Laser heat pulse was irradiated on the front side of cylindrical specimen (Ø12.5 × 3 mm), the heat is transmitted through the sample thickness direction and the resulting temperature rise at the sample's rear face is recorded as a function of time.

The higher the thermal diffusivity of the sample, the shorter the time needed to heat the opposite side of the sample.

Specific heat capacity was measured by differential scanning calorimeter. Thermal conductivity and can be obtained from following equation:

$$k = \alpha C_p \rho$$

where k is thermal conductivity, α is thermal diffusivity, C_p is heat capacity and ρ is density.

The thermal conductivity of a semi-crystalline polymer can be described by means of the modified Maxwell model, which assumes that a semicrystalline polymer is made up of anisotropic spherical crystallites imbedded in an isotropic amorphous matrix. The thermal conductivity will therefore be a function not only of temperature but also of the percentage of crystallinity of the polymer.

Table 11 PEEK Thermal Conductivity at 250°C

THERMAL CONDUCTIVITY @ 250°C	W/m-K	0,25
THERMAL CONDUCTIVITY @ 250°C	W/m-K	0,42

In fact, the first thermal cycle provides information on the product, thus considering the previous thermal history to which it was subjected prior to the analysis. The cooling cycle, on the other hand, makes it possible to analyze the behavior of the material during solidification. The slow and controlled cooling temperature allows the material to solidify in conditions that favor the rearrangement of the polymer chains in an ordered configuration. Finally, the second thermal cycle allows information to be obtained on the intrinsic properties of the material, since the influence of the thermal history of the product has been deleted during the melting that occurred at the end of the first cycle. From the graph the second heating cycle shows a similar trend to that shown for the first heating cycle, the melting peak has comparable amplitude and peak temperature between the two scans, however it was not possible to observe the cold crystallization peak in this case.

Looking at the cooling cycle, however thanks to the controlled cooling phase, the polymer chains of PEEK have sufficient time to organize themselves into ordered structures and thus generate crystalline domains. The crystallization peak is clearly visible in the cooling curve.

Focusing on the first heating cycle, an exothermic peak at 161 °C can be seen, which is attributable to the cold crystallization phenomenon. As the temperature increases, the polymer chains may become mobile enough to align themselves into further crystalline regions. When this happens, heat is released, and an exothermic peak is recorded by the instrument. From the graph, an endothermic peak is evident at 338°C, a peak caused by the melting of all the crystals in the sample. As would be expected, the endothermic peak is larger than the exothermic peak because the exothermic peak includes the combined energy to melt all the crystals formed, both during the previous thermal history of the material and during the DSC test. The percentage of crystallinity of the feed filament was found to be 36%.

Table 9 Summary of experimental data obtained through DSC analysis

T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (%)
146	338	47,5	0,5	36%

Coefficient of Thermal Expansion (α_T)

When a material in the solid state is subjected to cooling and/or heating cycles it has a tendency to contract/dilate. The phenomenon of expansion of bodies is directly related to the atomic bond force. In fact, by supplying heat to the System, the increase of the vibration amplitude of the atomic bond is favored, thus causing the dilation of the body. The greater the bond force, the lesser the expansion of the material.

The linear coefficient of thermal expansivity (α_T) is the length change for an infinitesimally narrow temperature range, at any temperature T, and is defined as follows:

$$\alpha_T = \frac{1}{L_0}\left(\frac{d\,L}{d\,\mathrm{T}}\right)_T$$

Where L is the length of the sample, T its temperature, and L_0 its initial length. The coefficient of thermal expansion therefore represents the correlation coefficient between the deformation undergone by the material and the temperature variation.

TECHNICAL DATA SHEET

Roboze PEEK

Thermogravimetric analysis (TGA)

PEEK has flame retardant properties and high thermal stability. TGA is an efficient method of studying the thermal decomposition temperatures of a material using a few tens of milligrams of the sample itself. By heating the material in a controlled atmosphere (pyrolytic conditions), temperature is the only factor influencing the decomposition of the material. However, in a fire scenario, the influence of oxygen on decomposition and combustion behavior should also be considered. In this case, the material is subject to thermo-oxidative degradation. It is therefore equally important to determine the thermal stability of the material in air. Therefore, the sample was analyzed in both inert and oxidizing atmospheres.

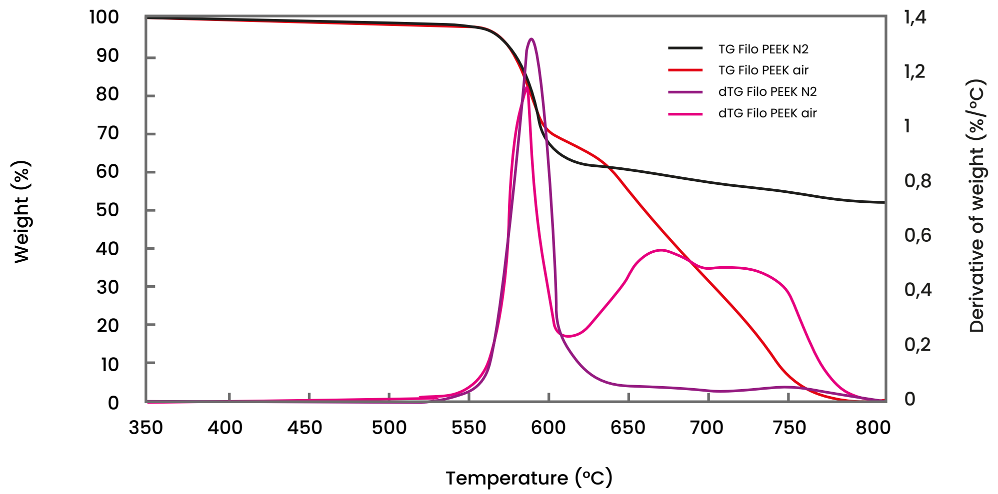

Table 10 TGA Spectrum of PEEK sample

In an inert atmosphere, the temperature of onset of thermal decomposition of PEEK (T_5%) was evaluated at 569°C and the maximum rate of mass loss (1.3%/°C) occurs at 583°C. At higher temperatures, the recorded mass loss is minimal. In fact, the final residual mass of PEEK at 800°C under nitrogen is 54%.

From this it can be deduced that the product formed during the pyrolysis of PEEK is quite stable in an inert atmosphere and at this temperature. It is known from the literature that PEEK is a polymer that tends to form carbon structures when subjected to pyrolysis. This suggests that during decomposition in nitrogen, the reaction that occurs leads to a thermodynamically stable carbonaceous structure.

When testing the sample in an oxidising atmosphere, the TG graph does not show any obvious temperature changes at the start of decomposition. This is evidenced by the temperature at which the sample records a 5% mass loss, which is similar to the previous case. From this, therefore, it can be deduced that the oxidative nature of the atmosphere in which PEEK is heated has little effect on the temperature at which it begins to decompose. This hypothesis is confirmed by looking at the temperature at which the peak mass loss occurs, which is similar to the previous case (582 °C).

However, the TG graphs also show that the presence of an oxidizing atmosphere modifies the decomposition mechanism which occurs at temperatures above 600°C. In fact, a non-zero DTG value is also observed at temperatures ranging from 605°C to 800°C .

This also suggests that the thermo-oxidative degradation of PEEK is at least a two-step process, one occurring at the beginning of decomposition, which involves the formation of a carbonaceous residue, followed by the slow oxidation of this carbonaceous residue at high temperatures.

TECHNICAL DATA SHEET

Roboze PEEK

Furthermore, it is interesting to note that at 800°C, only the TG graph of PEEK in nitrogen shows a certain residual mass of almost half the initial mass of the material. This means that the carbonized structure formed during the initial phase of thermal decomposition in the presence of oxygen tends to be completely oxidized by passing into a volatile phase at oxygen concentrations of 22%.

Glow Wire Test

Due to its excellent insulating properties and inherent flammability, PEEK is particularly used in the electronics industry. The Glow wire test is used to determine the ignition resistance of a polymer when it is brought into contact with an electrical resistor heated to a given temperature.

The highest temperature at which during three subsequent tests, flaming or glowing of the test specimen extinguishes within 30 seconds after removal of the glow wire without ignition of the indicator is called Glow wire flammability temperature (GWFI)

Table 12 Glow Wire Test of PEEK

PROPERTY	OPERATING CONDITIONS	UNIT OF MEASURE	VALUE	TEST METHOD
GLOW WIRE TEST – GWFI *	2mm THICKNESS	°C	960	IEC 60695-2-12

Electrical Properties

Surface Resistivity

Surface resistance is described as the ratio of a DC voltage to the current flowing between two electrodes that are in contact with the same surface of the specimen under test. The physical unit of surface resistance is Ohm (Ω). DIN IEC 60093 test method is used.

Table 13 Surface Resistance of PEEK

SURFACE RESISTANCE	DIN IEC 60093	>10^{12} Ω

Dielectric Costant

Electrical permittivity, also known as the dielectric constant, is a physical quantity that quantifies the ability of a material to withstand the intensity of the electric field inside it. From a mathematical point of view, it is possible to define the dielectric constant as a ratio, where the denominator is the capacitance of a capacitor using the material in question as a dielectric species, and the denominator is the capacitance of a similar capacitor using a vacuum as a dielectric. The dielectric constant value is a function of various variables such as frequency, operating temperature, and humidity. IEC 60250 is the test used to check the dielectric constant of PEEK.

Table 14 Dialectric Costant of PEEK

PROPERTY	CONDITIONS	VALUE	TEST METHOD
DIELECTRIC CONSTANT	23°C 1 KHZ	3,1	IEC 60250
DIELECTRIC CONSTANT	23°C 50 HZ	3,0	IEC 60250