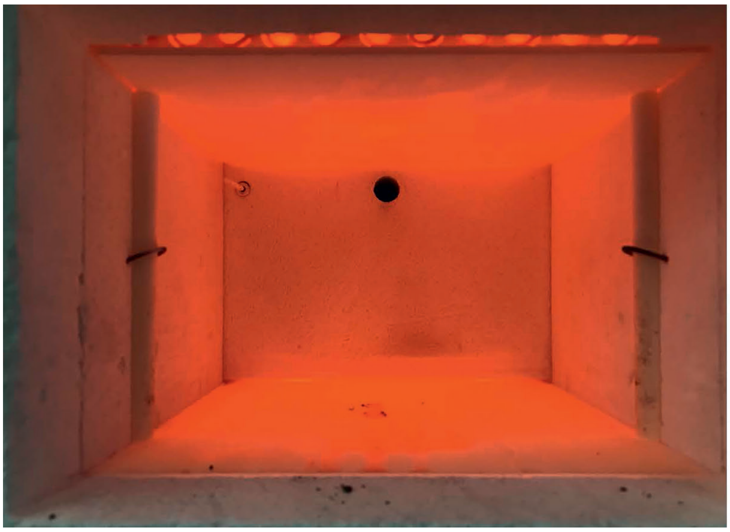

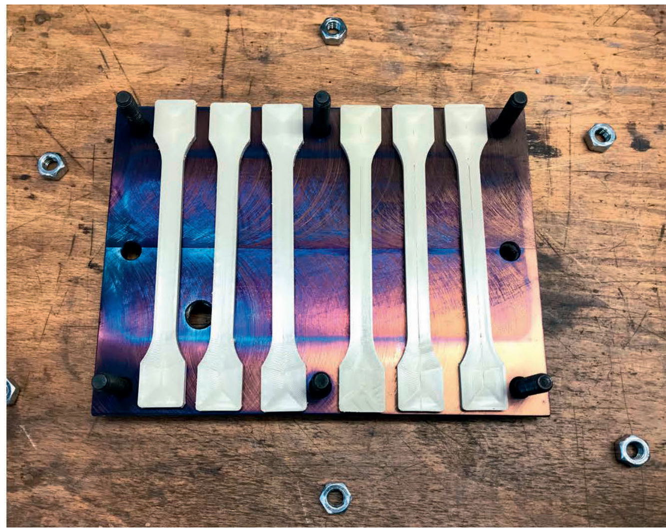

Increasing the degree of crystallization and improving the mechanical properties of 3D-printed PEEK tensile specimens (right) by post-heat treatment in a high-temperature furnace (left). © Dennis Prigann, PuK

Annealing of 3D-Printed High-Performance Polymers

Higher Crystallinity through Post Heat Treatment

The temperature management of formative manufacturing processes has a significant effect on the mechanical material properties of some semi-crystalline thermoplastics. The decisive factor is the plastic-specific degree of crystallization. In the case of producing parts by Fused Filament Fabrication, the degree of crystallization is relatively low, resulting negative influences on the mechanical properties. Targeted post heat treatment (annealing) allows 3D-printed parts to post-crystallize, which re-optimizes strength afterwards.

In terms of crystallinity, semi-crystalline thermoplastics can differ fundamentally from one another. On the one hand, they have different maximum degrees of crystallization that can be achieved under ideal processing conditions. On the other hand, they differ in terms of the temperature range above the glass transition point and below the melting point, in which the crystallization takes place. These two characteristics are present in semi-crystalline thermoplastics in very different manifestations. In addition, there is no causal relationship between these characteristics. For example, low-melting plastics can have a low or high degree of crystallization compared to high-melting plastics. This also applies conversely. For processing, it is therefore essential to know the material-specific properties of these thermoplastics exactly.

Compared to purely amorphous thermoplastics, semi-crystalline thermoplastics have a crystalline proportion in which the macromolecules form crystallites under certain conditions. A specific temperature range is required for this. During crystallization, molecules arrange themselves into regular, densely packed crystal structures due to the energetically more favorable material condition, depending on a sufficient period of time [1]. The attainable degree of crystallization depends on the molecular structure of the respective plastic and is limited by the maximum packing density. Crystallinity specifications indicate the percentage of the crystallized volume (**Table 1**) [2].

High Degree of Crystallization for High Strength

The increase of the crystallized volume leads to higher strength values and an equally higher temperature resistance due to intermolecular forces [2, 6]. In dependency of the glass transition and melting temperature, the degree of crystallization of semi-crystalline thermoplastics is influenced by the formative manufacturing processes. Polyoxymethylene (POM), for example, has a glass transition temperature around –60 °C [7]. This means that this plastic can still crystallize at room temperature if the theoretically possible degree of crystallization has not been reached under processing conditions. Semi-crystalline thermoplastics with higher tem-

(Semi-crystalline) thermoplastic	Typical degree of crystallization
Polyamide (PA)	~35-60 %
Polyethylene terephthalate (PET)	~30-40 %
Polyetheretherketone (PEEK)	~30-50 %
High density polyethylene (HDPE)	~60-80 %
Low density polyethylene(LDPE)	~40-55 %
Polyoxymethylene (POM)	~70-80 %
Polypropylene (PP)	~50-80 %

Table 1. Typical crystallization degrees of selected semi-crystalline thermoplastics Source: [3–5, 8]

Printing parameters	Value
Extrusion temperature	400 °C
Print bed temperature	140 °C
Build chamber temperature	80 °C
Nozzle diameter	0.4 mm
Extrusion muliplier	1.05
Layer height	0.2 mm
Infill	80 %
Printing speed	1200 mm/min

Table 2. Applied printing parameters for FFF printing of PEEK. Source: Dennis Prigann, PuK

perature requirements, such as polyamides (PA), lacks this potential. Because the glass transition temperature for PA 6 is in the range of 50 to 60 °C, a correspondingly higher temperature range is required for crystallization [8]. Post-crystallization in the room temperature range is therefore excluded. Depending on the temperature management, the degree of crystallization can vary [9]. If complete crystallization is to be achieved, this can be implemented either by slow cooling during processing or post heat treatment processes (annealing).

Post Heat Treatment to Increase Crystallinity

Semi-crystalline thermoplastics can be annealed to increase the degree of crystallization. Annealing means tempering above the glass transition temperature and below the melting temperature. A renewed melting of crystalline areas is thereby not provided. Due to the molecular excitation through thermal energy, the freedom of molecular motion increases to such an extent that both the degree of crystallization and the crystal size can further increase [10, 11].

Compared to conventional plastics processing, the following aspects are particularly critical for Fused Filament Fabrication (FFF) in this context:

- Relatively high cooling rates, which can limit the achievable degree of crystallization for 3D-printed parts.
- Tool-free shaping, which eliminates the existence of mold temperature control, one of the most important functions of conventional manufacturing processes.

If it is an FFF printer with a closed build chamber, the material is exposed to the temperatures in the build chamber after it exits the nozzle. In addition to the closed or open chamber design, commercial 3D printer systems differ in the heat output of the build chamber and build platform. Depending on the respective FFF printer and the mass temperature of the extruded plastic melt, higher or lower temperature gradients can be expected.

Crystallization Degree of 3D-Printed PEEK

The crystallization behavior of polyetheretherketone (PEEK) was investigated as part of a research study at the Institute for Polymer Materials and Plastics Technology at the Technical University of Clausthal, Germany. PEEK is one of the most common high-performance polymers and is used for example in the automotive or aerospace industries. It is a semi-crystalline thermoplastic and has a crystallization degree of up to 48 % [8]. The high processing temperatures are particularly challenging in FFF printing. PEEK is printed at temperatures around 400 °C. The manufacturer's recommen- »

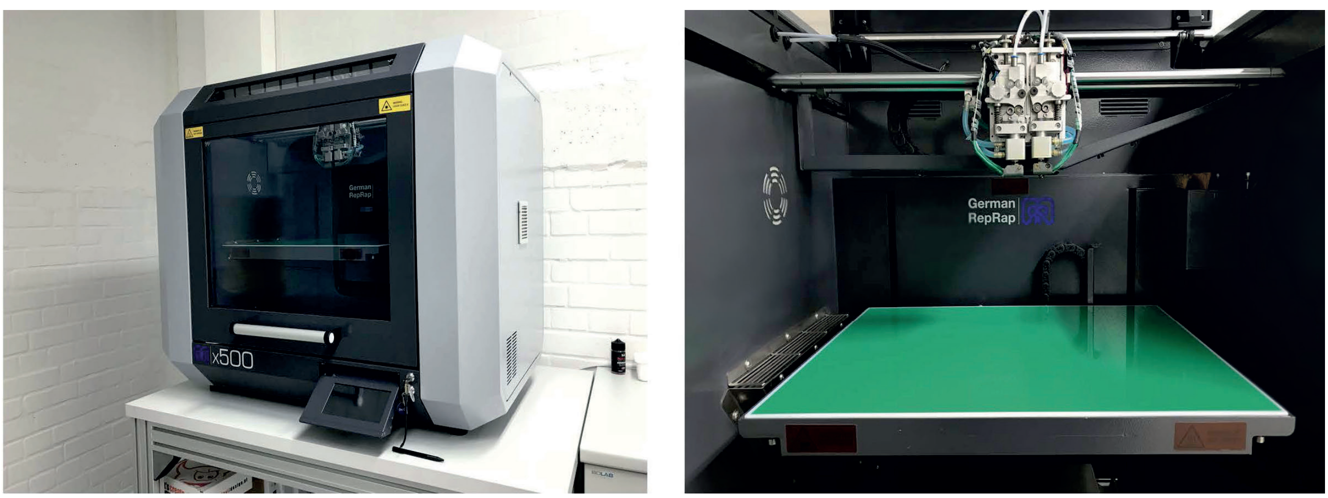

Fig. 1. An FFF printer x500 from RepRap was used to print the examined PEEK samples. © Dennis Prigann, PuK

dations are 130 to 145 °C for the build platform and 70 to 140 °C for the build chamber [12]. The glass transition temperature of PEEK is in comparison to that around 145 °C [8]. The chamber temperatures during printing are therefore below the glass transition temperature of the polymer. The temperature range required for this plastic to crystallize is therefore only passed through in the course of cooling. Whether the resulting cooling rate is sufficient has not yet been clarified.

With the differential scanning calorimetry (DSC), PEEK under ideal temperature control and 3D-printed PEEK based on temperature-related manufacturer recommendations (FFF print parameters, **Table 2**) were compared together. The polyetheretherketone was printed with the FFF printer x500 from the manufacturer German RepRap (**Fig. 1**). As can be seen from the results, the FFF printing process under mentioned conditions is insufficient for the complete crystallization of this high-performance polymer (**Fig. 2**).

Strength Values with and without Post Heat Treatment

For comparison purposes, other parts were printed and post-tempered using a annealing process in the Nabertherm LT 15/12/B180 muffle furnace (**Title figure**). Within this process the plastic is heated up to 150 °C at a rate of 25 °C/h and maintained for 2 h (homogenization). The material was then heated up to 200 °C at the same heating rate, with also the same holding time of 2 hours. Finally, the printed parts were cooled down to room temperature at a cooling rate of approximately 30 °C/h (**Fig. 3**). The results of the DSC illustrate the effectiveness of the post heat treatment (**Fig. 4**). The crystallization degree of the 3D-printed PEEK shows comparable values to those of the ideal controlled material due to post-crystallization in a high-temperature oven.

It has been proven that the degree of crystallization can be increased by post heat treatment (annealing). The next step was to investigate how the mechanical strength of the various 3D-printed PEEK parts differed. For this purpose, printed tensile specimens were tested using a ZwickRoell 1445 universal testing

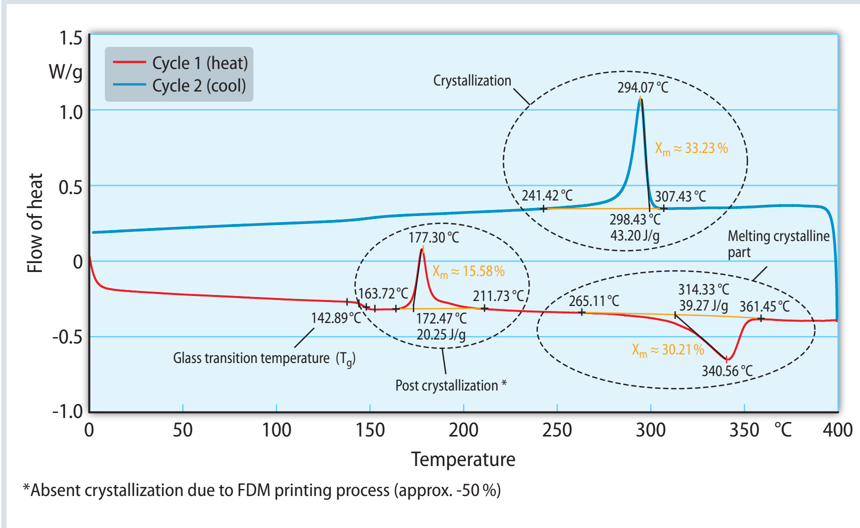

Fig. 2. DSC analysis of a 3D-printed PEEK according to the manufacturer's recommendations: in FFF printing some polymers does not crystallize completely (X_m = degree of crystallization). Source: Dennis Prigann, PuK; graphic: © Hanser

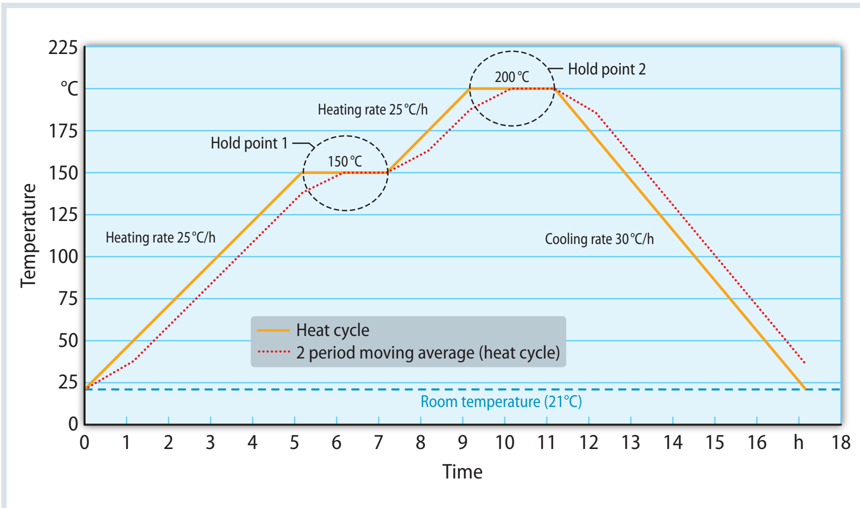

Fig. 3. Annealing process for 3D-printed PEEK parts from the FFF printer: in this process, the material is first heated to 150 °C, maintained at this temperature for 2 hours and then heated up again to 200 °C. Source: Dennis Prigann, PuK; graphic: © Hanser

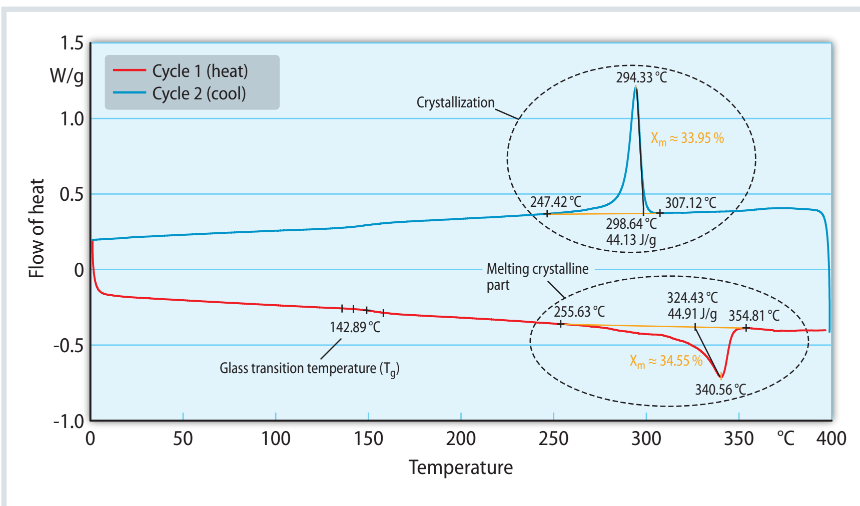

Fig. 4. DSC of FFF printed and post-heat-treated PEEK: post-treatment increases the degree of crystallization. Source: Dennis Prigann, PuK; graphic: © Hanser

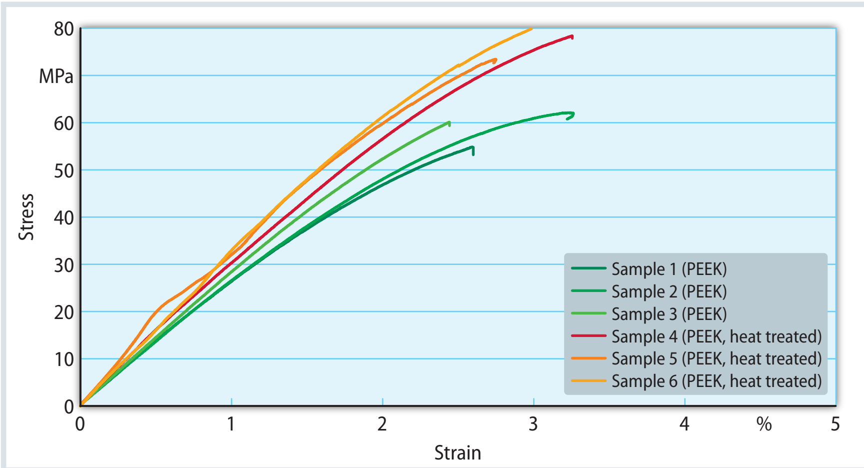

Fig. 5. Comparison of the strength values of FFF printed PEEK tensile samples with and without post-heat treatment: the post-treatment improves the mechanical properties. Source: Dennis Prigann, PuK; graphic: © Hanser

machine under uniaxial tensile stress in accordance with the DIN EN ISO 527–1 standard. The annealed tensile specimens show significant increases in strength compared to the non-heat-treated ones (**Fig. 5**):

- The modulus of elasticity increases by up to 22 %.
- Tensile strength increases by up to 34 %.
- Elongation increases up to 29 %.

Because the post heat treatment of 3D-printed PEEK was limited to a maximum of 200 °C, the improved tensile strength due to optimized layer adhesion by melting the edge areas can be excluded. Therefore, increasing the degree of crystallization through post heat treatment is directly related to optimizing strength at the macromolecular level.

Conclusion

Material-specific post heat treatment can be used to optimize the strength values of certain semi-crystalline thermoplastics processed in 3D printing (FFF). Subsequent tempering above the glass transition temperature and below the melting temperature leads to significant increases in strength, especially for polymers with higher crystalline proportions, if this has not yet been achieved procedurally.

In this context, it is important to know the ideal temperature control of the processed thermoplastics. Lower cooling rates could be achieved, for example, by much higher build chamber and build platform temperatures. Nevertheless, the cooling process has to be examined even then more precisely. ■

Info

Text

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References & Digital Version

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