

PROCESSING POLY(ETHER ETHERKETONE) ON A 3D PRINTER FOR THERMOPLASTIC MODELLING

OBDELAVA POLYETHER ETHERKETONEA NA 3D-TISKALNIKU ZA TERMOPLASTIČNO MODELIRANJE

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PEEK, poly(ether etherketone), is one of the high-quality industrial polymers. It is widely used in extremely demanding areas like automotive, aircraft and space industries. Because of the fact that it is bio-compatible, PEEK is also used for medical implants that are usually made by milling a block of the material. The article presents the results of an investigation of processing PEEK on a 3D printer for thermoplastic modelling. The used procedure is one of the additive manufacturing procedures and, as such, it builds a product by adding material layer by layer to get the finished product. Commercially available machines are unable to achieve the required melting and environment temperatures, so a new machine was developed. The machine was designed and built at the company Ortotip d.o.o. and it is able to produce the parts of up to 130 mm × 130 mm × 150 mm. After the initial testing, test specimens, according to standards EN ISO 527-2: 2012 and EN ISO 178: 2011, were produced and tested at the facilities of the PEEK manufacturer Invio (from the UK). The article presents the steps taken when developing the PEEK modelling machine, the test methods to verify the mechanical properties of manufactured products and the results of the material testing. The machine was developed to produce medical implants (specific maxillofacial prosthesis), but with additional testing (that will help to improve the mechanical properties of produced parts) practically all bone-replacement implants can be made.

Keywords: PEEK, 3D printer, implant, medical application, thermoplastic, FDM, biocompatible, additive technology

PEEK, polyether etherketon, je eden izmed visoko kvalitetnih industrijskih polimerov. Uporablja se na zahtevnih področjih, kot so avtomobilska, letalska in vesoljska industrija. Zaradi dejstva, da je biokompatibilen, je uporaben tudi za medicinske vsadke, ki so navadno narejeni s frezanjem iz bloka materiala. Članek predstavlja izsledke raziskave oblikovanja PEEK s 3D-tiskalnikom za termoplastično modeliranje. Uporabljen postopek spada med tako imenovane dodajalne tehnologije in kot tak gradi izdelek po slojih. Komercialno dostopni stroji ne zmorejo doseči zahtevanih procesnih in okoljskih temperatur, zato je bila razvita nova naprava. Ta je bila oblikovana in izdelana v podjetju Ortotip, d. o. o., in je primerna za izdelke do velikosti 130 mm × 130 mm × 150 mm. Po uvodnih preizkusih so bile izdelane preizkusne epruvete v skladu s standardoma EN ISO 527-2: 2012 in EN ISO 178: 2011 in preizkušene od proizvajalca PEEK-materiala Invio (iz VB). Predstavljeni so ključni koraki pri razvoju naprave za direktno izdelavo modelov, preizkusne metode za verifikacijo mehanskih lastnosti izdelanih kosov in rezultati meritev. Naprava je bila razvita za izdelavo medicinskih vsadkov (posebno lobanjske vsadke), vendar bo ob dodatnih preizkusih (za izboljšanje mehanskih lastnosti izdelanih kosov) primerna za vse vrste medicinskih vsadkov.

Ključne besede: PEEK, 3D-tiskalnik, vsadek, medicinska aplikacija, termoplast, FDM, biokompatibilnost, dodajalne tehnologije

1 INTRODUCTION

Today the majority of long-lasting human-body implants are made from three materials. The first is the bone cement, to technicians more known as poly(methyl methacrylate) – PMMA. Its great advantage is that it can be processed during the operation since it can be made of two components (liquid and powder) that are mixed together and directly processed (by hand or with some basic tools) in a short time (the curing time can be as short as 2 min). The production of the implants made from solid PMMA is used only in special cases like the lens for trabeculum. The second material is titanium (actually one of the titanium alloys) that is processed with a conventional machining process (usually the CNC milling or turning) or with one of the additive manufacturing procedures like SLM (selective laser melting),¹ MLSS (metal-laser-sintering system)² or EBM (electron-beam melting).³ After a long-term use titanium shows some problems,⁴ but it is irreplaceable when

excellent mechanical properties are needed. The material that promises the most is PEEK – poly(ether etherketone). The implants from PEEK⁵⁻⁷ are usually made with the conventional machining process or the method, presented in 2010, of direct manufacturing with an SLS (selective laser sintering) machine.⁸ Since PEEK is thermoplastic it can be formed also with the other procedures that are widely used for other thermoplastics.⁹ The challenges are the specific requirements relating to a higher viscosity (**Figure 1**) that need to be taken into consideration, so the idea of developing a dedicated device (a 3D printer for thermoplastic modelling) was born.

2 BASIC PRINCIPLES OF THE 3D PRINTER FOR THERMOPLASTIC MODELLING

The 3D printer for thermoplastic modelling is basically an FDM (fused-deposition modelling) machine. As

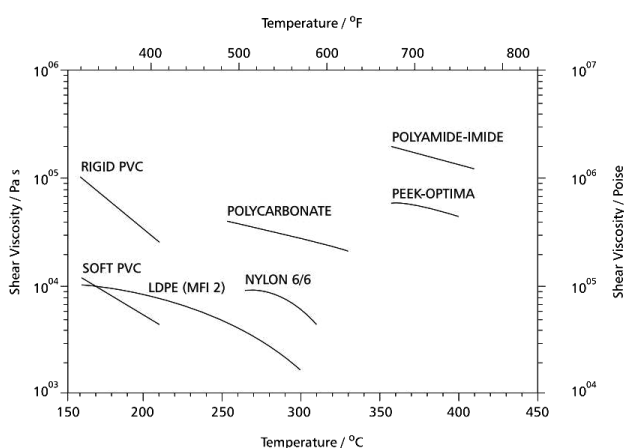


Figure 1: Shear viscosity versus the temperature for some common, industrial, engineering thermoplastics, comparable to PEEK Optima[®] LT1⁹

Slika 1: Viskoznost v odvisnosti od temperature za nekaj termoplastov v široki uporabi v primerjavi z PEEK Optima[®] LT1⁹

any additive manufacturing procedure (also known as the rapid prototyping)^{10–14} it starts with a 3D CAD model that is usually exported as an STL file from a CAD (engineering or dedicated medical) program. The STL file is then sliced by the computer software into horizontal layers that are as high as the layer in the machine. The rod-shaped filament is supplied to the machine through a nozzle. The nozzle is computer controlled in the X, Y plane and, in one layer, it forms a raster of the item in the respective layer. The material is liquefied in the nozzle and it hardens quickly when applied to the layer at a lower temperature. The entire system must be preheated to a higher surrounding temperature. After the layer is finished, the working bed in the Z direction is lowered by the thickness of one layer and the new layer is extruded. When the geometry of a part is more complex¹⁵ (overhangs), a support structure must be added.

3 MACHINE DESIGN

The machine design was based on the 3D printer Ciciprinter¹⁶ presented in 2011 and was made with the CAD program Solid Works. In the prototypes the open-source control electronics¹⁷ and the software made for RepRap printers¹⁸ were used, with a simple adaptation, to achieve the desired application. The basic principle of thermoplastic modelling stays the same, but there are completely different requirements for industrial or medical machines, comparable with the distinction between home-used or educational tools. For medical equipment, standard ISO 13485¹⁹ is valid and for electronic circuits, several other guidelines (like 89/392/EEC, 73/23/EEC and 89/336/EEC) need to be taken into consideration. PEEK, like most of the widely used thermoplastic materials (ABS, HDPE, LDPE, etc.), is not easy to process and in order to get the best results,

the manufacturer's instructions⁹ must be followed. The basic material properties were studied and discussed with the material supplier to get the data of the processing parameters for a small-nozzle extrusion.

At this point the decision was made to develop a PEEK printer that uses a rod-shaped material rather than a more classical approach with the grains and an extrusion screw because of the required screw length, a need for an expensive regulation equipment (pressure measurements and electronic valves) and a requirement for cleaning after the completion of each batch (which, in the case of a unique or small-series production, means practically every day).⁹

For the testing purposes the first machine with a heating chamber was produced (**Figure 2**). The heaters with a combined power of 1000 W were used to preheat the working plate to around 240–300 °C. The first problem was the implementation of a mobile platform inside the chamber that required a mechanism for an accurate movement in the Z direction with a minimum loss of heat. The soft isolation and the central holder for the platform were eventually used. The second problem was how to assure the movement in the XY direction of the nozzle and prevent the heat loss at the top of the chamber. The known industrial solution with protective bellows would be an elegant solution, but the working

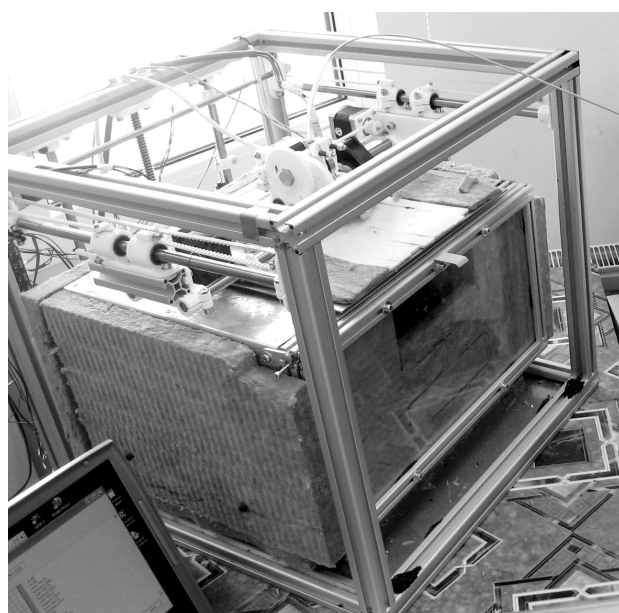


Figure 2: First laboratory PEEK machine. On the top there is an extruder mechanism with the 1 : 5 thrust ratio from the small NEMA 17 step motor to the specially shaped stainless-steel thrust screw. The PEEK rod diameter of 2.2 mm (± 0.1 mm) was routed from the nearby roll. The maximum chamber temperature was only around 300 °C because of the 1000 W heat source and a poorly applied insulation.

Slika 2: Prva preizkusna naprava za predelavo PEEK-a. Na vrhu je mehanizem za podajanje materiala z razmerjem 1 : 5 in pogonskim koračnim motorjem NEMA 17. Pogon je izveden preko nazobčanega pogonskega vijaka iz nerjavnega jekla. PEEK-žica, premera 2,2 mm ($\pm 0,1$ mm), je bila speljana iz koluta v bližini. Zaradi grelnikov 1000 W in slabe izvedbe izolacije je bila najvišja dosežena temperatura komore samo okrog 300 °C.

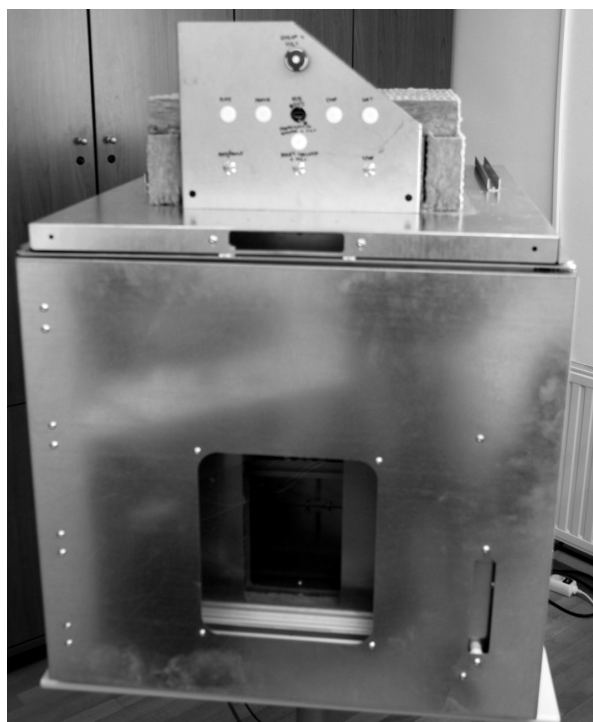


Figure 3: PEEK2 machine with a better insulation, more powerful heaters, a preheated chamber for the material and a new and improved electric controller

Slika 3: PEEK2-naprava z izboljšano izolacijo, močnejšimi grelniki, komoro za predgretje materiala in novim, izboljšanim električnim krmiljem

temperature was simply too high, so a movable insulated panel was used. The design of the hot-end part, together with the extrusion nozzle, required another special solution. The hot end is the part where the melting process takes place, so it needs to be insulated from the hot-end holder to prevent the heat transfer through the leading pipe that could cause the material melting in the leading pipe and the subsequent blockage of the material at the next start. Some tests were made with ceramic or composite materials,^{20–22} but, at the end, the nozzle was thermally separated from the holder with a thermal barrier made on the leading pipe in the shape of narrowing/ thinning walls.

The second machine (**Figure 3**) was designed with all the updates that had been developed in practice after the previous tests. The working chamber was insulated with a thicker insulation and was more carefully closed so that the heat losses were, subsequently, lower than before. The building chamber was increased to allow a more equal air heating and a bit larger building volume, especially in the Z direction. With the use of more powerful heaters, the preheating time needed to reach the working temperature (now set at 280 °C to 300 °C) was shortened from more than one hour to 20 min. The extrusion tests also showed a need for a new hot-end design, so the hot end with a bayonet mechanism for a fast and simple exchange was made.

4 MATERIAL PROPERTIES

The PEEK supplier Invibio prepared two different PEEK Optima® materials – LT3 and LT1. The properties of both materials,²³ for the case of injection moulding, can be found in **Table 1** and the shear viscosity versus the shear stress at different temperatures is presented in **Figure 4**. When used in the injection-moulding process, LT3 has slightly higher mechanical properties and a lower viscosity and as such it should be ideal for our application.

Table 1: Mechanical properties of the PEEK Optima® LT1 and LT3 materials processed with injection moulding²³

Tabela 1: Mehanske lastnosti PEEK Optima® LT1 in LT3 materialov, izdelanih z brizganjem v forme²³

Property	Units	LT1	LT3
Melt viscosity	(kN s)/m ²	0.44	0.16
Density	g cm ⁻³	1.3	1.3
Tensile strength (Yield)	MPa	100	108
Tensile elongation (Break)	%	40	25
Flexural strength	MPa	165	170
Water absorption (24h)	%	0.5	0.5
Melt temperature	°C	340	340
Mould shrinkage	%	1.2	1.3

5 PRELIMINARY TESTS

The first tests were made with PEEK LT3 on a simple extrusion device. Those tests just confirmed the possibilities of processing PEEK in the desired way (extrusion through a small nozzle). **Figure 5** presents the results of the first extrusion test that, due to a short delivery time, was made with an industrial PEEK form another manufacturer.²⁴ The first extrusion was successful, so during the next steps the first PEEK 3D printer (shown previously on **Figure 3**) was constructed.

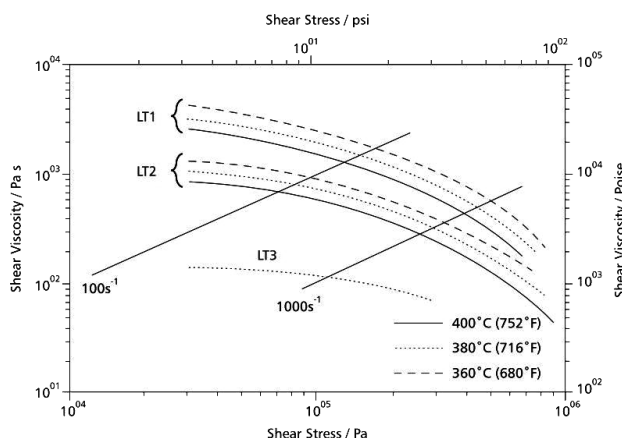


Figure 4: Shear viscosity versus shear stress at different temperatures shows that PEEK Optima® LT3 has a significantly lower viscosity when compared to LT1 or LT2⁹

Slika 4: Viskoznost v odvisnosti od strižne napetosti in temperature kaže na nižjo viskoznost PEEK Optima® LT3 v primerjavi z LT1 ali LT2⁹

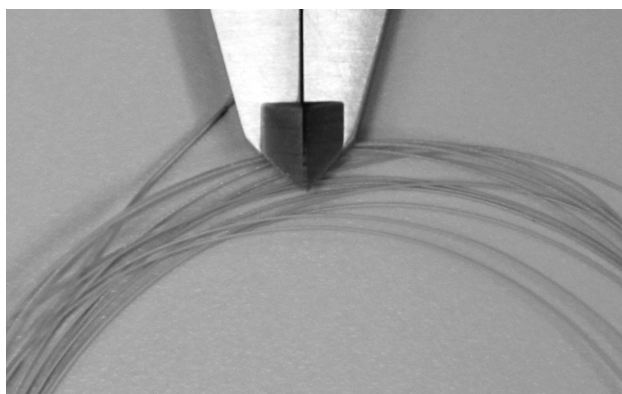


Figure 5: First extrusion tests showed that an extrusion of PEEK through a small-diameter nozzle is possible

Slika 5: Prvo poizkusno ekstrudiranje je pokazalo, da je ekstrudiranje PEEK-a skozi šobo majhnega premera mogoče

After the approval of the possibility of using the extrusion principle, the first PEEK processing machine was made and the first parts were produced. After several



Figure 6: Degradation of PEEK inside the nozzle as a result of several heating cycles. The left figure shows the inside of the nozzle after being used for 15 cycles (15 working days). The right figure shows small particles that are caused by the material degradation inside the nozzle and are eventually deposited onto the product.

Slika 6: Razgradnja PEEK-a v šobi kot rezultat večkratnega segrevanja. Leva slika prikazuje notranjost šobe po 15 ciklih (15 delovnih dneh). Na desni sliki so vidni majhni črni delci, ki so se pojavili v izdelku kot posledica razgrajenega materiala, ki je iz notranjosti šobe prehajal v izdelek.

Table 2: Test settings of the TA Instruments Q2000 differential scanning calorimeter

Tabela 2: Nastavitve TA-naprave Q2000 za diferenčno vrstično kalorimetrijo

Parameter	Value
Number of cycles	5
Sampling interval	0.20 s/pt
Equilibrate temperature	30.00 °C
Ramp 1	20.00 °C/min to 400.00 °C
Isothermal	2.00 min
Mark end of cycle	0
Ramp 2	20.00 °C/min to 30.00 °C
Isothermal	5.00 min
Mark end of cycle	0
Ramp 3	20.00 °C/min to 400.00 °C
Mark end of cycle	0

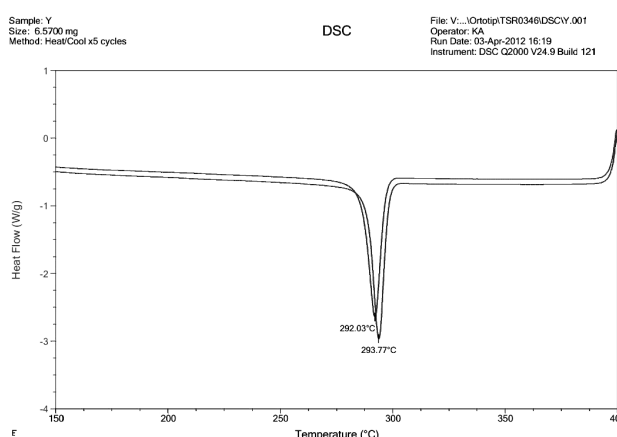


Figure 7: Results of the differential scanning calorimeter. Set-A traces show the first and the fifth crystallisation cycles.

Slika 7: Rezultati diferenčnega vrstičnega kolorimetra. Sledi seta A prikazujeta prvi in peti cikel kristalizacije.

production cycles some problems with the material thermal decomposition inside the extrusion nozzle appeared (**Figure 6**).

To verify the cause of a degraded polymer, additional tests were made. The presence of a degraded polymer was performed using a TA Instruments Q2000 differential scanning calorimeter with the settings presented in **Table 2**.

The results (**Figure 7**) of a multi-cycle DSC analysis did not indicate the presence of a degraded polymer. The difference between the first and the last recrystallization cycles was approximately 1.7 °C. If a degraded polymer had been present, the value (difference) would have been significantly larger, at least 5 °C to 10 °C. It is, therefore, likely that the bubbles are due to the presence of the moisture in the polymer when the sample specimens were made.

To get the best possible results, the material was dried again (according to the manufacturer,⁹ the LT3 material should be dried for at least 3 h at 150 °C or 12 h at 120 °C) and a new, clean extruder was used for the sample production.

6 PROCESSING DATA AND TEST PROCEDURES

According to the standards EN ISO 527-2: 2012 plastics – determination of tensile properties and EN ISO 178: 2011 plastics – determination of flexural properties, several sets of test specimens were made (**Figure 8**). Optical microscopy was performed using an Olympus SZX7 optical microscope and the Spot imaging software. The tensile-strength testing was performed on an Instron 3367 tensometer using the InVibio laboratory test method INV-LAB-TM12 revision 2. SEM was performed on a Hitachi TM3000 scanning electron microscope.

The SEM analyses of the gaps and voids (**Figure 9**) showed a presence of moisture even after the raw material was dried according to the material manufacturer's

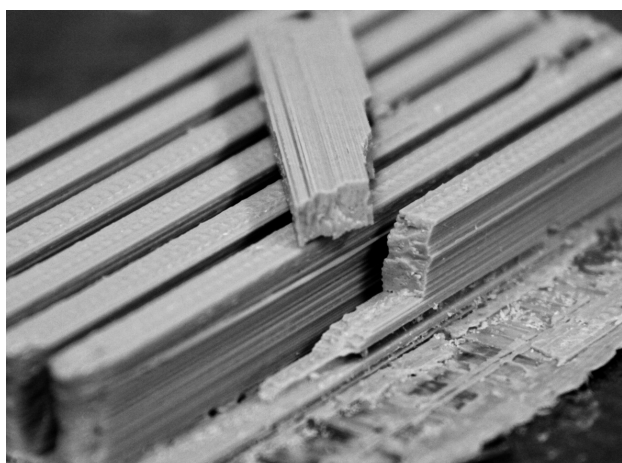


Figure 8: PEEK test specimens made on the PEEK plate. A nicely fulfilled structure is seen and so are the layers in the Z direction.

Slika 8: PEEK-preizkusni vzorci, izdelani na delovni plošči iz PEEK-a. Vidi se lepo izpopolnjena notranja struktura in sloji v Z-smeri.

data. The problem is that it takes several hours to produce a set of samples, so the material gains the moisture back from the surrounding air. The results lead us to improve the design of the PEEK printer and include a drying chamber, so that the material can be in dry condition all the time.

The results of the tensile stress showed that the tensile strength of the parts made with the presented technology (thermoplastic modelling or FDM) is significantly lower (**Figure 10**) than the results for the parts made with injection moulding (**Table 1**). However, the tensile strength is still high enough for designated applications (higher than for the implants made of PMMA).

To test the impact of heat treatment (present due to a long production time) on the product, the test specimens were produced and left in the chamber at a high tempera-

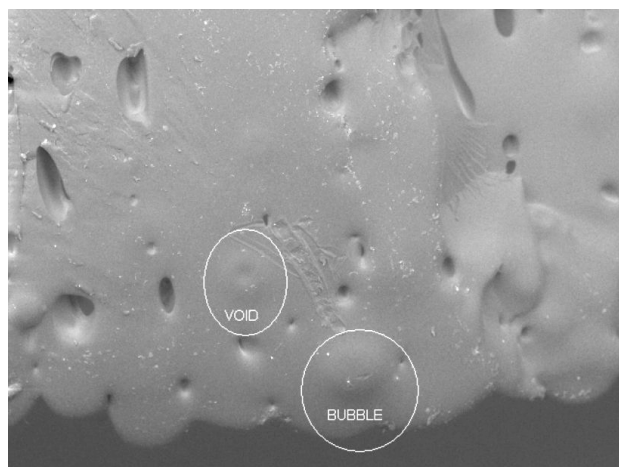


Figure 9: Gaps and bubbles in the model are a result of the moisture in the material

Slika 9: Vrzeli in mehurčki v izdelku so posledica vlage v materialu

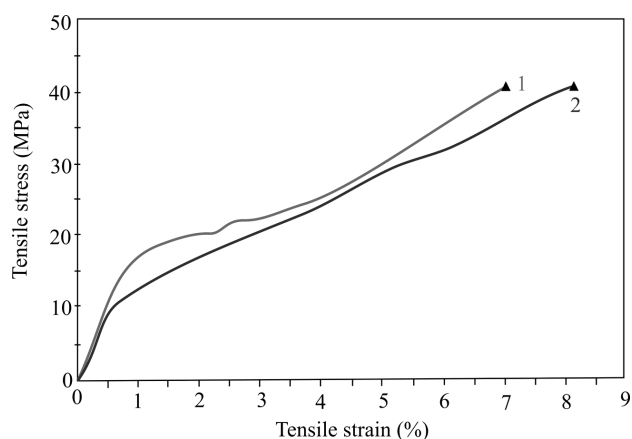


Figure 10: Typical response of a PEEK specimen. After trimming the second PEEK printer, the average tensile stress of approximately 60 MPa can be achieved for the large parts that are taken out of the production chamber immediately after the end of the production.

Slika 10: Značilen diagram preizkušanja mehanskih lastnosti. Po nastavitvi parametrov na drugem PEEK-tiskalniku je mogoče doseči natezno trdnost okrog 60 MPa, če so deli odstranjeni iz delovne kore takoj po končani izdelavi.

ture for additional 12 h. The results (**Figure 11**) showed it has a negative impact on the mechanical properties that should be avoided, so the parts should be taken out of the chamber immediately after the production.

The last test presents the problem of a non-uniform raw material that was delivered (**Figure 12**). These test specimens showed that a change in the rod diameter from 2.3 mm to 2 mm (in the case of the first delivered charge, resulting in a material deficit in volume of 30 %) can cause a drop in mechanical properties of up to 50 % (**Figure 13**).

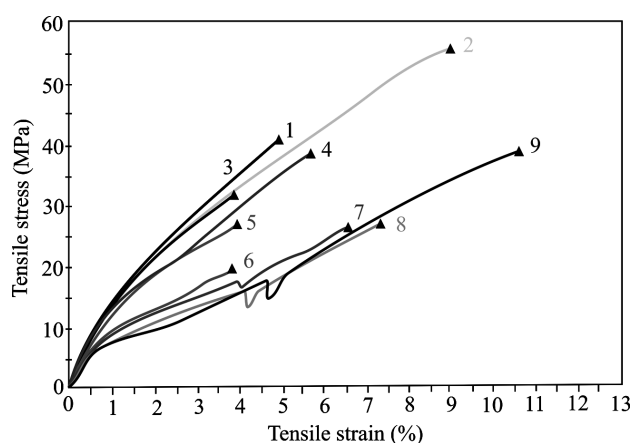


Figure 11: Response of the test specimens after being left in a heated environment for 12 h. Mechanical properties of the products under the obligatory high temperature are deteriorating with time. The colour change from light brown to dark brown was also detected. Specimens 2 and 9 have unusually high values, so they are excluded from the average-value calculations.

Slika 11: Diagram preizkusnih vzorcev, zadržanih na visoki temperaturi okoli 12 h. Mehanske lastnosti izdelkov se zaradi vpliva visokih temperatur hitro slabšajo. Opaziti je tudi spremembo v barvi izdelkov, od svetlo rjave na temno rjavo. Vzorca 2 in 9 imata nenavadno visoke vrednosti, zato pri izračunih srednje vrednosti nista bila upoštevana.

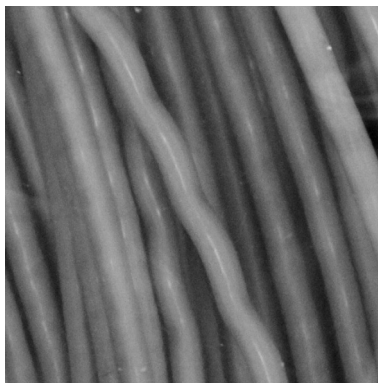


Figure 12: Non-uniform raw rod varying from 2 mm to 2.3 mm in diameter presents a big problem, since it leads to a lack of the material inside the produced part and, subsequently, to a drop in the mechanical properties.

Slika 12: Neenakomeren prerez osnovnega materiala, ki variira med 2 mm in 2,3 mm, je velik problem, saj povzroči pomanjkanje materiala v izdelku in posledično slabše mehanske lastnosti.

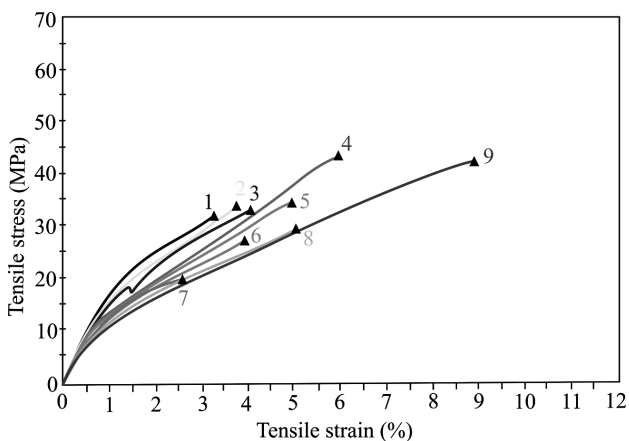


Figure 13: Drop in the mechanical properties as a result of the change in the diameter of the rod from 2.3 mm to 2 mm

Slika 13: Poslabšanje mehanskih lastnosti kot posledica spremembe premera žice iz 2,3 mm na 2 mm



Figure 14: Thin-wall tornado (the wall thickness of only 0.55 mm) produced from LT3 PEEK

Slika 14: Tankostenski tornado (debelina stene samo 0,55 mm), izdelan iz materiala PEEK LT3

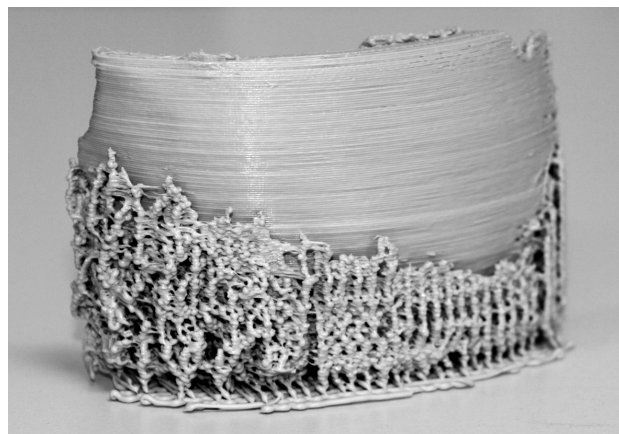


Figure 15: Part of a real-shape implant (a skull implant) made with the support material in the vertical position

Slika 15: Del lobanjskega vsadka, izdelanega z dodatnimi podporami v pokončnem položaju

7 PRODUCTS

For additional tests and calibration three basic shapes were used: a cube to get the right amount of the extruded material, a cylinder to check the X and Y movement synchronisation and a test specimen according to the standards (ISO) for mechanical properties. The goal of the 3D printer is to produce more complex shapes, so real-life products (also in the shapes of implants) were also produced. **Figure 14** presents one of the first successfully produced bigger parts (a height of 100 mm) with a really small wall thickness, due to poor mechanical properties later replaced by the LT3 PEEK Optima® material. **Figure 15** shows one of the latest parts in the shape of a real-size (a width of approx. 120 mm) skull implant with a support structure. The implant was made in the vertical position since we found that in this position smoother products can be made.

8 CONCLUSION

The article presents only a small amount of the research done in the project to make a 3D printer capable of directly producing PEEK parts. In the process of developing the appropriate device, several other products were made. The PEEK printer is currently in its final prototype phase, it is functional but to produce a part, additional knowledge on the part orientation, machine tricks and G-code generation is still needed. Because of the bio-compatibility requirement, the whole hot end (the part where PEEK changes the aggregate state from solid to liquid) is exchangeable and must be exchanged after a part has been produced. The hot end is then renewed at the manufacturer's facility.

Future development is planned to improve the mechanical properties, so some more tests with appropriate building temperatures and speeds need to be done. The next step is also to replace the control electronics with

robust, accurate and reliable home-made electronics developed specially for this application (so additional parameters will be monitored and, if needed, more powerful motors can be used).

Acknowledgement

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