MECHANICAL PERFORMANCE OF LASER SINTERED POLY(ETHER KETONE KETONE) (PEKK)

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Abstract

The recent progress in Additive Manufacturing Powder Bed Fusion systems are bound to attract uptake of new high performance materials. Within the Poly(aryl ether ketone) (PAEK) family, Poly(ether ketone ketone) (PEKK) shows promising mechanical properties, comparable with the commercial laser sintering grade PEK HP3, whilst processed at significantly lower temperatures. Kepstan 6002 PEKK specimens were laser sintered in multiple orientations and a range of mechanical tests were used to assess overall performance. PEKK showed outstanding ultimate tensile strength ranging between 75 and 90 MPa in x-y direction whilst maintaining an elongation at break of 2.6%. Further investigation of the fracture showed localized plastic regions attributed to a better performance. The same plastic behaviour is observed during compression, in which PEKK showed remarkable deformation with no signs of breaking. The combination of properties offered by Kepstan PEKK parts manufactured at a lower processing temperature makes it a very attractive polymer for applications in the aerospace and automotive sectors.

Keywords: High temperature laser sintering, PEKK, mechanical performance.

1   Introduction

Recent advances in additive manufacturing (AM) are continuously expanding the application of this technology to multiple industries with a variety of needs. Laser sintering (LS), the most popular powder bed fusion process, allows serial production of unique parts with attractive mechanical and thermal performance [1, 2], hence offering wider application range. This technique uses a laser as a heat source to fuse or sinter polymer particles on a preheated powder bed according to the 2D representation provided with the slicing. This process is repeated layer-by-layer until the desired 3D object is completed [3].

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LS is widely employed to produce polyamide 12 (PA12) parts with excellent mechanical resistance and dimensional accuracy, but remains a challenge for other materials with promising applications, especially in medical, automotive and aerospace industries in which higher mechanical performance, lightweight, biocompatibility, chemical resistance, temperature stability and flame retardancy are desirable properties. Poly(aryl ether ketone)s (PAEKs) attend those needs and are promising candidates already being employed in traditional manufacturing to replace metallic parts in several applications such as implants, knee or hip replacement [4, 5], structural components for aircrafts and automotive industry, engine blocks [6] and piston components [7].

Within the PAEK family, poly (ether ketone ketone) (PEKK) is a new grade being explored in LS. The structure is similar to Poly(ether ether ketone) (PEEK), however the polymerization is different as PEKK is produced by electrophilic acylation reaction from diphenyl ether (DPE), terephthalic acid (T) with para phenyl links and isophthalic acid (I) with meta phenyl links [8]. Different concentrations of T and I links change the structure of the polymer, and most importantly, the kinetics of crystallization. Furthermore, by increasing the I linkage, the melting temperature can be significantly reduced, hence preventing degradation [9] but also enabling manufacturing at lower bed temperatures, an attractive factor for powder recycling.

Whilst PEK HP3 requires processing temperatures above 350 $^{\circ}$C to avoid part warping and poor mechanical performance, PEKK can be processed almost 100°C below. This makes it suitable for newer systems such as EOS P 500, P 800, P 810 [10] and LSS Raptor [11].

Few studies provided some mechanical data for PAEKs specimens produced by High Temperature Laser Sintering (HT-LS). Ghita et al. [7] investigated tensile strength and elongation at break of PEK HP3 produced using EOS P 800. They achieved 90 MPa of ultimate tensile strength (UTS) and 3.7% of elongation at break for the virgin PEK HP3 manufactured in X orientation. Berretta [12] used the same equipment to produce tensile specimens of Victrex PEEK 450PF; they obtained 67 MPa of UTS in X orientation.

More recently, Hoskins et al. [13] investigated other mechanical properties of PEK HP3 manufactured with EOS P 800, including flexural strength, fracture toughness, compression strength and modulus. The fracture of tensile specimens showed brittle behaviour with secondary fractures and a smooth failure plane. For compressive tests, delamination was observed followed by deformation, and the fractures contained partially sintered material. Indeed, several studies [1, 14, 15] reported a significantly lower elongation at break for the same material manufactured by LS in comparison with injection molding (IM); this is attributed to the anisotropic nature of the LS process and the poor adhesion between layers.

The present study is the first to provide a comprehensive set of mechanical data of Kepstan 6002 PEKK for LS. Parameters were optimized to achieve the best mechanical performance in all manufacturing orientations. Tensile, flexural and compression tests were performed and compared with other PEEK grades available. Surface roughness was measured to support the mechanical properties of PEKK and two different platform temperatures were used and compared regarding final mechanical performance.

2 Materials and Methods

2.1 Materials

The PEKK grade used in this study was supplied by Arkema as Kepstan 6002 PEKK [16]. This grade was prepared from diphenyl ether, terephthalic acid (T) and isophthalic acid (I) at a concentration T/I of 60/40 [8]. The mechanical data produced was compared with EOS

PEK HP3 [17] and Victrex PEEK 450PF [18]. General information of each of these grades are provided in Table 1 and Table 2.

Table 1: Properties of different PAEKs powder for LS.

Grade	Glass transition temperature, T_g [°C]	Melting temperature, T_m [°C]	Density of solid parts [g/cm^3]
Kepstan 6002 PEKK[16]	160	300	1.27*
PEK HP3[17]	164	372	1.32
PEEK 450PF[18]	143	343	1.30

*Value referred to amorphous Kepstan PEKK 6002.

Table 2: Particle size and distribution of different PAEKs powder for LS.

Grade	Average particle size $(D_{50,3})$ [μm]	$D_{10,3}$ [μm]	$D_{90,3}$ [μm]
Kepstan 6002 PEKK[16]	52.8	33.35	87.87
PEK HP3[17]	60	36.52	88.08
PEEK 450PF[18]	50	-	-

2.2   Laser sintering

Kepstan 6002 PEKK was processed using EOS P 800 HT-LS system [19]. Samples were built in different orientations (X, Y and Z) as shown in Figure 1 using two different platform temperatures (265 °C and 286 °C). The location of the platform and process chamber temperatures in the LS system are shown in Figure 2. Process chamber temperature refers to the temperature at the top layer of the build provided by the infrared heaters. The building platform temperature refers to the temperature around the powder bed (bottom and sides - exchangeable build frame temperature). The specimens were produced in the reduced building configuration, which constrains the area of fabrication to one-third of the total area available for manufacturing. Previous to this work, LS specimens were produced using different combinations of laser parameters to optimize the process. The best combination of parameters were applied as shown in Table 3.

PEK HP3 and PEEK 450PF grades show a visible super-cooling window at a standard DSC rate of 10 °C/min [20]. On the contrary, Kepstan 6002 PEKK does not show a recrystallization peak at standard dynamic cooling rates (typical if processed via injection moulding) but crystallizes when processed by LS. This is the reason why two different platform temperatures were tested, one above and the other within crystallisation range for PEKK [8].
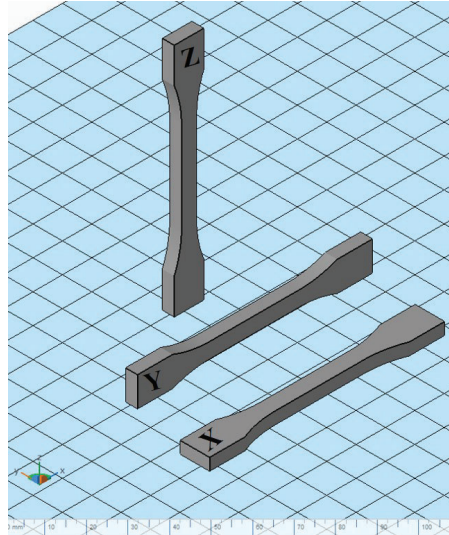
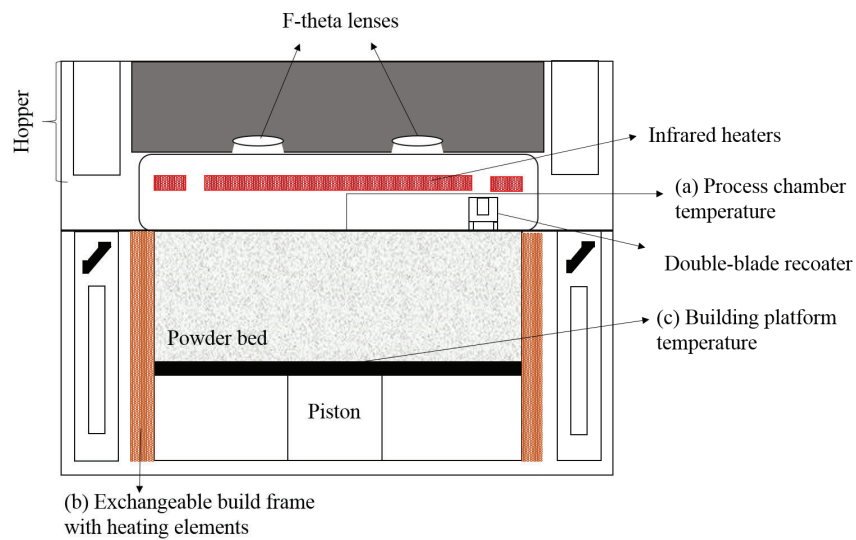Figure 1: Illustration of different manufacturing orientations in laser sintering.

Figure 2: Schematic illustration of EOS P 800 system. (a) Process chamber temperature; (b) exchangeable build frame temperature and (c) building platform temperature.

Table 3: Process parameters applied for laser sintering of PEKK.

Parameter	Value
Energy density (hatching)	23.5 mJmm^{-2}
Layer thickness	120 μm
Process chamber temperature	292 $^{\circ}$C

2.3 Differential scanning calorimetry

DSC experiments were performed to investigate the melting temperature of PEKK and thus determine the appropriate processing temperatures of this polymer in the EOS P 800 system. Three samples from 5 mg to 10 mg of PEKK were placed in 40 μL aluminium pans and taken to analysis in a Mettler Toledo 821e/700 equipment with a nitrogen flow rate of 50 ml/min. The samples were heated and cooled at a standard 10 $^{\circ}$C/min rate from room temperature to 400 $^{\circ}$C.

2.4 Mechanical testing

The mechanical properties of Kepstan 6002 PEKK was assessed under tensile, flexural and compressive behaviour following the ISO guidelines shown in the following sections.

2.4.1 Tensile testing

Tensile testing was performed using a Shimadzu AGX-plus equipment with a maximum force of 2 tonnes. A total of ten specimens for each orientation and temperature were tested at 1 mm min^{-1} following ISO 527-2-1BA standard. The calculation of elastic modulus considered a deformation of 0.2% in the elastic region.

2.4.2 Flexural testing

Flexural behaviour was investigated using a Lloyd EZ20 equipment at a three-point bending configuration, according to ISO 178 for plastics. A test speed of 1 mm min^{-1} was chosen and ten specimens for each orientation were tested.

2.4.3 Compressive testing

Compressive testing was performed following ISO 604 guidelines. The test used a Lloyd LR 300K equipment operating at 5 mm min^{-1}. Ten specimens of 10 mm in diameter were manufactured for each orientation, X and Z. The chosen limit for compressibility was of 75% of the specimens' height regardless of failure being identified.

2.5 Scanning electron microscopy

SEM analysis was performed to investigate fracture behaviour and propagation. Images were captured using a Tescan Vega3 scanning electron microscope at the accelerating voltage of 10 kV and current of 0.13 nA. The samples were coated with 10 nm thick gold to avoid charging.
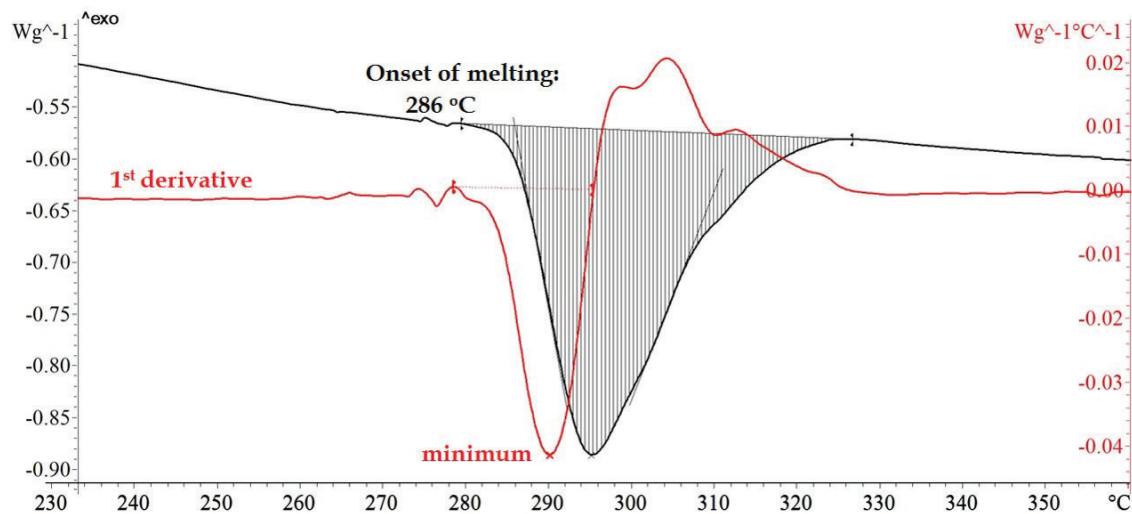
Figure 3: DSC heating thermoscan of Kepstan 6002 PEKK indicating melting and the first derivative of the melt.

3   Results and discussion

3.1   Determining processing temperatures

To avoid warping or geometrical distortions, semi-crystalline polymer powders are pre-heated to what is referred to as the building temperature [21]. For polyamides, this temperature is in the super-cooling window, known as the area between melting and recrystallization peaks [22]. For PAEKs, additional heat is provided by the infrared heaters after melting induced by the laser; this is known as the post-sintering time. Berretta et al. [20] developed a methodology for multiple grades of PAEKs in which the process chamber temperature corresponds to the minimum of the first derivative obtained from the melt peak of DSC thermoscans. In Figure 3, the same method was performed for Kepstan 6002 PEKK. The measurement was repeated three times and the average temperature, 292 °C, was selected for the infrared heaters.

Due to the amorphous behaviour of PEKK when cooled at standard DSC rates, two building platform temperatures were chosen. The first considered the average between melting peak temperature and maximum rate of crystallization temperature (220 °C to 240 °C) [8]; this corresponds to approximately 265 °C. The second building platform temperature was chosen as the onset of the melting peak, which is roughly 286 °C. By prolonging the time of PEKK in amorphous phase (above crystallization temperature), we believe elongation can be improved as time for flow and coalescence is increased.

3.2   Mechanical properties

3.2.1   Tensile strength testing

The tensile tests results of Kepstan 6002 PEKK specimens manufactured at different orientations and a building platform temperature of 265 °C are shown in Figure 4.

Similar to other materials processed by LS, Kepstan 6002 PEKK specimens were greatly affected by anisotropy, performing significantly better in X orientation. This orientation gives the best ultimate tensile strength (UTS) and elongation at break of, respectively, 90 MPa and 2.6%. The worst performance is found in Z orientation as a result of the poor adhesion between
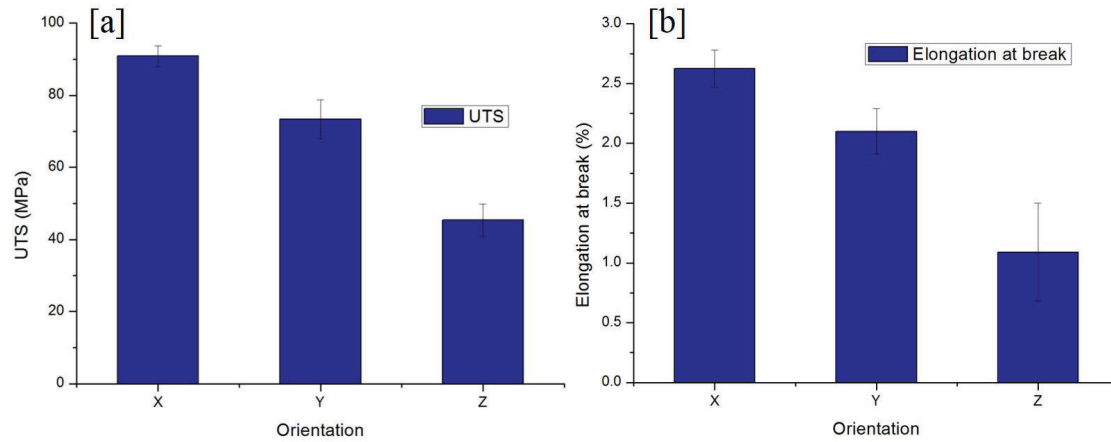
Figure 4: [a] Ultimate tensile strength and [b] elongation at break of Kepstan 6002 PEKK manufactured in different orientations.

layers, supported by a flat failure and low elongation. For these specimens, the UTS was 50% lower than the values achieved in the X orientation, whilst elongation was reduced by almost 60%.

Figure 5 shows a comparison of [a] UTS and [b] elongation at break of PEKK specimens processed in different orientations and building platform temperatures, as described in Section 3.1. The specimens produced at 265 °C had their best performance when manufactured along X orientation.
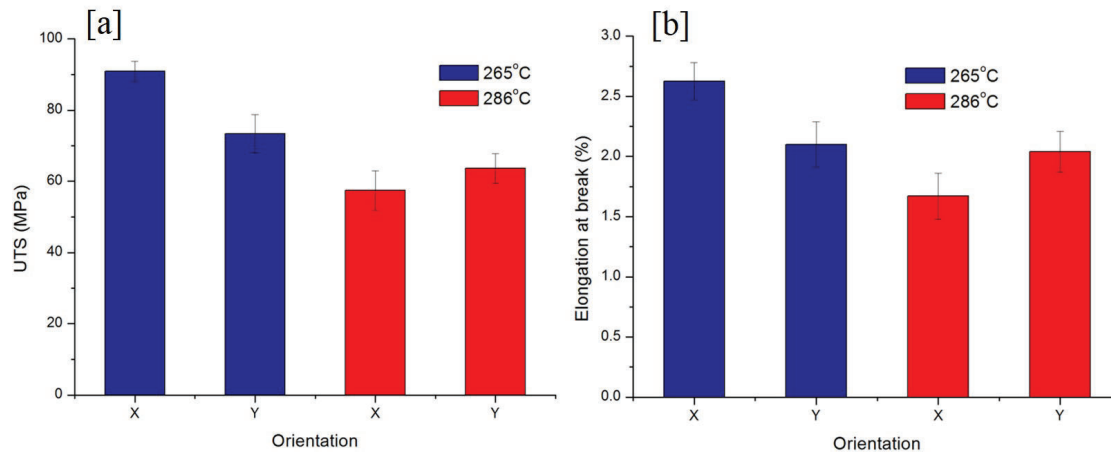

Figure 5: [a] Ultimate tensile strength and [b] elongation at break of Kepstan 6002 PEKK specimens processed at different building platform temperatures.

With the increase in building platform temperature, mechanical strength is significantly reduced as well as elongation at break. A combination of factors can explain these results: crystallisation, surface roughness and porosity of the specimens. Considering the results shown in Figures 4 and 5, additional mechanical tests were performed only on samples manufactured at a building platform temperature of 265 °C.
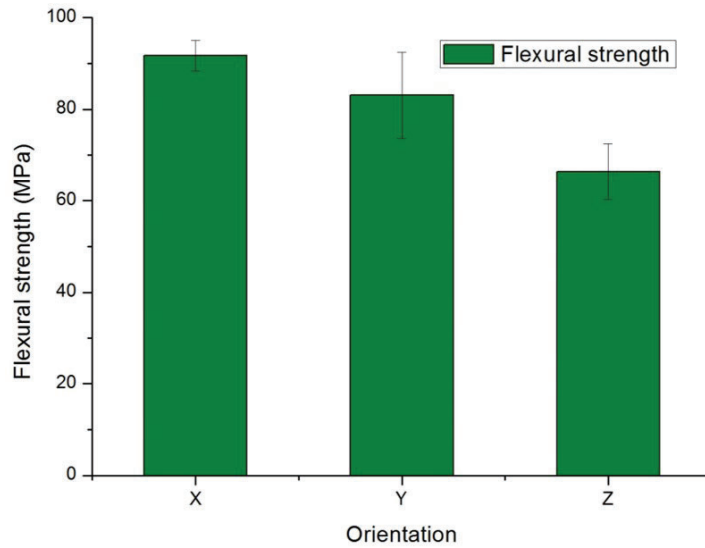
Figure 6: Flexural strength of Kepstan 6002 PEKK manufactured in different orientations.

3.2.2 Flexural strength testing

Flexural strength was assessed for specimens manufactured in all orientations (see Figure 1) at a building platform temperatures of 265 $^{\circ}$C, as shown in Figure 6. The specimens in Z orientation showed a significant drop in strength in comparison with X and Y orientation. This difference in strength with orientation suggests heterogeneity in the structure caused by the lower adhesion between layers in Z orientation and the presence of defects in the specimens.

3.2.3 Compressive strength testing

Compressive tests were carried out in Kepstan 6002 PEKK specimens manufactured at a building platform temperature of 265 $^{\circ}$C, in X and Z orientation. The results are shown in Figure 7 and Table 4. PEKK showed outstanding plastic behaviour and most specimens remained unbroken even at 70% of deformation, as observed in Figure 7. Due to the high deformation, strength can be difficult to assess, therefore the curve was separated in three regions: (i) elastic, (ii) plastic deformation up to 50% and (iii) plastic deformation between 50% and 75%. The compressive strength achieved in the elastic region, at 20% deformation, was of 168 ± 10MPa, comparable to what reported by Hoskins [13] for PEK HP3. However, Kepstan 6002 does not break at the end of the elastic region, but shows an outstanding plastic behaviour, deforming up to 75% of the original thickness with no signs of delamination. At this compression, Kepstan 6002 PEKK shows an average stress of 557 MPa in Z orientation, whilst specimens in X orientation reached 734 MPa of compressive strength. This behaviour has never been observed for LS PAEKs before.

3.3 Fracture investigation

To understand the reasons for failure, the fracture surface was examined using SEM as shown in Figure 8. At 500x magnification, ductile regions are observed in localized regions of the fracture for specimens manufactured in X orientation. This plastic behaviour seems to be holding the specimens together for a longer period, thus increasing elongation and overall performance despite being at localized areas. Such regions were not observed in any other
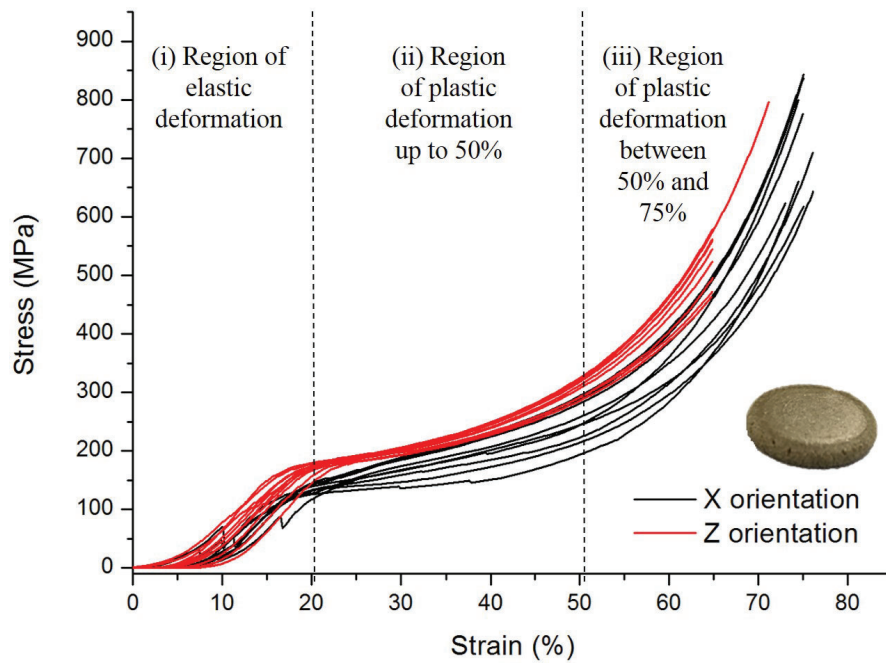
Figure 7: Compressive strength of PEKK manufactured in different orientations at a building platform temperature of 265 °C and a specimen after compression.

orientation (Figure 8[c] and [d]), or at higher building platform temperatures, e.g. 286 °C. The mechanical performance results support the idea that increasing the area of plastic zones in the fracture improves elongation at break and tensile strength.

The edges of compressive specimens which showed small cracks were examined as well and are presented in Figure 9. The plastic regions are quite clear at 1000x magnification, supporting the high deformation found for Kepstan 6002 PEKK.

4   Conclusions

This study provides a first comprehensive set of mechanical performance for LS Kepstan 6002 PEKK. By optimizing the laser parameters and testing two different building platform temperatures, Kepstan 6002 PEKK achieved a tensile strength of 90 MPa and elongation at break of 2.6%. Due to the anisotropic behaviour of most materials processed by LS, tensile strength and elongation at break of Z specimens were reduced by 50% of the performance achieved in the X orientation; similar results are found with flexural testing. When compressed, Kepstan 6002 PEKK showed outstanding plastic behaviour, deforming up to 75% with no evidence of delamination or shatter. Hoskins et al. [13] measured compressive strength for LS PEK HP3 and achieved 184 MPa, slightly above the compression strength found for PEKK in the elastic region, but only 33% of the strength found for PEKK when deformed plastically up to 70% (built in Z orientation). Kepstan 6002 PEKK shows promising mechanical performance with slightly higher tensile strength than PEK HP3 and similar elongation at break as reported in Table 5.

Choosing the appropriate process chamber temperature and especially building platform temperature is crucial as it relates with polymer crystallisation kinetics and time for coalescence, therefore significantly changing mechanical properties.

Table 4: Compressive properties of LS PEKK.

Property	Orientation/ Percentage strain	Value
Compression modulus (GPa) [ISO 604]	X	0.13 ± 0.007
Compressive strength (MPa) [ISO 604]	X/75%	734.8 ± 93.8
	X/20%	134.4 ± 8.9
	Z/70%	557.2 ± 93.8
	Z/20%	168.3 ± 10.6

In summary, Kepstan 6002 PEKK shows very promising suitability for HT-LS by achieving similar performance to EOS PEK HP3 but being processed at lower temperatures, therefore enabling powder recycling and reducing cost. These results can be further optimized through careful correlation with the kinetics of crystallization of PEKK [8] to increase the plastic zones in the specimens and improve mechanical properties.
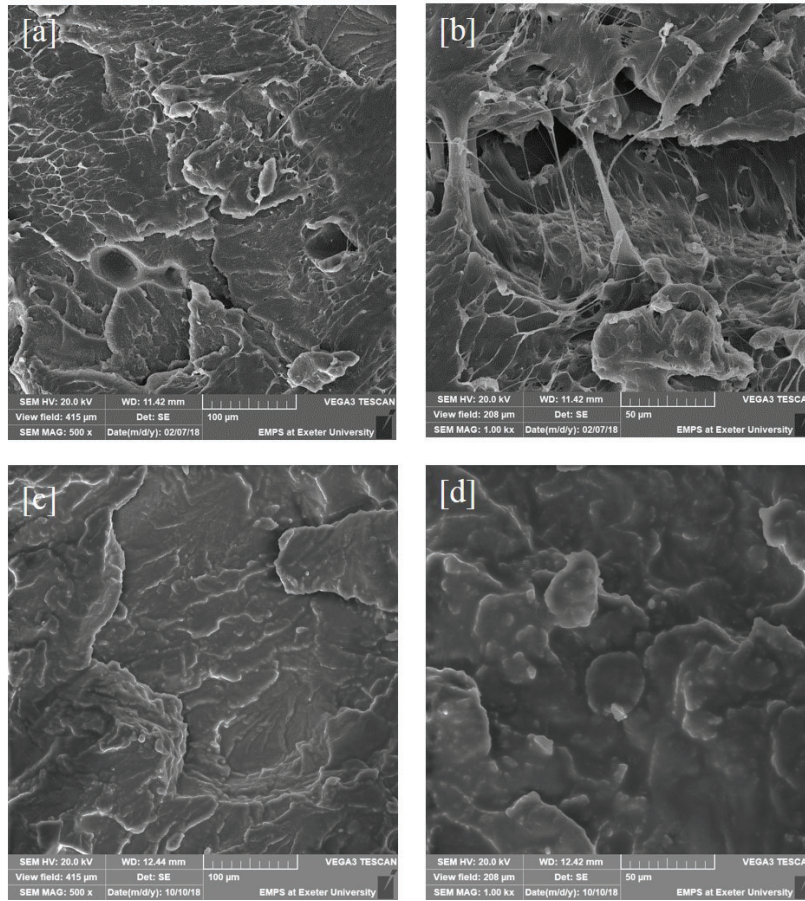
5   Acknowledgements

Figure 8: Fracture images of Kepstan 6002 PEKK processed at 265 °C in [a-b] X and [c-d] Z orientation.
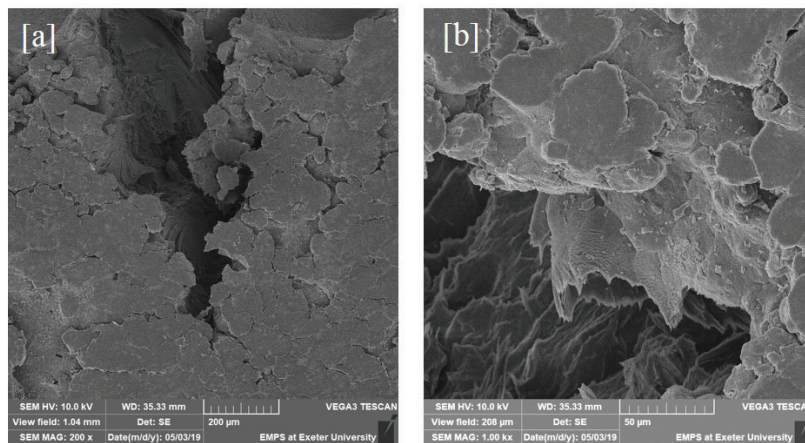

Figure 9: SEM investigation of compressed specimens of Kepstan 6002 PEKK built at a platform temperature of 265 °C in the X orientation.

Table 5: Mechanical properties of different PAEKs processed using laser sintering.

Material	Kepstan 6002 PEKK	PEK HP3	PEEK 450PF
Tensile modulus (GPa) [ISO 527]	X: 4.6 ± 0.3	X: 4.3 ± 0.2 [17]	–
	Y: 4 ± 0.1	–	–
	Z: 3.9 ± 0.4	–	–
Tensile strength (MPa) [ISO 527]	X: 90.9 ± 2.9	X: 90 ± 5 [17]	X: 67 ± 4 [23]
	Y: 73.4 ± 5.4 [24]	Y: 79.3 ± 5.5 [24]	–
	Z: 45.4 ± 4.5	Z: 44.3 ± 3.1	–
Elongation at break (%) [ISO 527]	X: 2.6 ± 0.2	X: 2.7 ± 0.2 [17]	–
	Y: 2.1 ± 0.2	Y: 3.8	–
	Z: 1.1 ± 0.4	Z: 1.5	–
Flexural strength (MPa) [ISO 178]	X: 91.7 ± 3.4	–	–
	Y: 83.1 ± 9.4	–	–
	Z: 66.3 ± 6.1	–	–
Compression modulus (GPa) [ISO 604]	0.13 ± 0.007	0.61 ± 15 [13]	–
Compressive strength (MPa), at different percentage strain [ISO 604]	X-Y [75%]: 734.8 ± 93.8	–	–
	X-Y [20%] 134.4 ± 8.9	–	–
	Z-X [70%] 557.2 ± 93.8	–	–
	Z-X [20%] 168.3 ± 10.6	184 ± 15 [13]	–

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