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Enhanced Surface Integrity of a Biomedical Grade Polyetheretherketone through Cryogenic Machining

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Abstract

Polyetheretherketone (PEEK) belongs to a group of thermoplastic polymers widely used in bioengineering applications such as trauma, orthopedic and spine implants, whose mechanical and geometrical characteristics, when put in service, must be the highest possible. However, machining operations, usually carried out for their manufacturing, can assure these characteristics uniquely when they are performed in a restricted temperature window because of the PEEK mechanical behavior change nearby its glass transition temperature.

To this aim, the present paper investigates the feasibility of using cryogenic machining to enhance the surface integrity of a biomedical grade PEEK. Turning trials were carried out under dry and cryogenic machining conditions at varying feed and cutting speed. The temperature reached during the process was measured by means of a thermocouple embedded in the cutting tool, whereas the surface integrity assessed in terms of surface defects, surface roughness and hardness. Additionally, the degree of crystallinity was evaluated via Differential Scanning Calorimetry (DSC). To correlate machinability results with the PEEK mechanical behavior, tensile tests were performed in the temperatures range between - 100°C and 50°C.

The obtained results showed that the application of liquid nitrogen always made possible achieve an enhanced surface integrity compared to the corresponding dry condition, which represent the currently used strategy for the manufacture of biomedical polymer implants. A proper temperature control during machining assured indeed the formation of lower amounts of defects as well as reduced surface roughness, by increasing the PEEK degree of crystallinity.

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Keywords: Cryogenic, machining, polymer, temperature, surface finish, surface integrity.

1. Introduction

Machining can represent a valid alternative to injection or extrusion molding when low production volumes or high dimension accuracy of polymer parts are required, as is in the biomedical field. Nevertheless, machining of polymers is challenging due to their temperature-dependent behavior, which makes them rapidly lose stiffness at increasing temperature. Further, the application of traditional coolants to favour heat removal during cutting is not suitable in the case of biomedical polymers due to oil residuals they leave on the surface. The issue of heat removal is especially true in the case of Poly(aryl-ether-ether-ketone) (PEEK), which is widely exploited for the manufacturing of spinal implants, femoral

stems, or as a bearing material in orthopaedic implants [1]. PEEK, in fact, has a low coefficient of conductivity, thus encounters difficulties in heat dissipation.

Cryogenic machining in general, and cryogenic cooling in particular, may represent a solution when carried out on polymers, as they assure clean machined surfaces and significant heat removal.

Dhokia et al. [2] exploited liquid nitrogen to freeze Ethylene-Vinyl Acetate (EVA), characterized by a glass transition temperature equal to -44°C, before machining. They demonstrated the feasibility of machining personalised shoe insoles thanks to the hardening given by this under machining below room temperature before machining.

Kakinuma et al. [3] evaluated the feasibility of adopting

micro-machining under cryogenic conditions as alternative to photolithography and micro-moulding to manufacture microfluidic chips. These parts are usually made PolyDiMethylSiloxane (PDMS), characterized by a glass transition temperature equal to -123 °C, and therefore difficult to cut in virtue of its low elasticity at room temperature. It was shown that by means of cryogenic machining the microgrooves could be machined precisely. The same Authors in [4] evaluated the dimensional accuracy of the machined grooves thermal considering the PDMS shrinkage, demonstrating the feasibility of using cryogenic machining in the manufacturing of bent holes, which are extremely difficult to obtain with conventional machining processes.

Aldwell et al. [5] cooled the Ultra-High Molecular Weight Polyethylene (UHMWPE), characterized by a glass transition temperature of -125°C, by submerging it in liquid nitrogen for one day before machining. They found that the workpiece under machining increased the workpiece stiffness and improved the surface quality; nevertheless, the improvements were inferior with respect to the ones given by other cutting parameters.

Bertolini et al. [6] evaluated the machinability of polyammide 6 (PA6), whose glass transition temperature is 20°C, under cryogenic cooling, showing that smoother and harder surfaces were obtained when machining in cryogenic machining conditions than when machining under conventional flood.

To date several attempts have been made on evaluating cryogenic machining of polymers, but none of them has focused on PEEK, which has a glass transition temperature above the room one. On this basis, in the present research work, cryogenic machining was evaluated as an alternative to dry cutting in machining biomedical grade PEEK, at varying cutting parameters. The surface integrity was assessed in terms of surface roughness, surface defects, crystallinity degree and hardness. Finally, to explain the experimental outcomes, tensile tests at different temperatures were performed and correlated to the cutting temperature measured during the process.

2. Experimental

2.1. Material

The investigated material is the TECAPEEKTM supplied by Ensinger Plastics. It is a biomedical grade material used for biomedical applications like posterior spine stabilization rods in spinal trauma, interference screws for repairing the cruciate ligaments and fixators for meniscal tears, and abutments in dental prostheses. It was purchased in form of a bar of 42 mm diameter and 1000 mm length. The material was received in the annealed state, which was conducted at 221°C for 4 hours. Annealing is usually processed in order to have a dimensionally stable material during machining.

The PEEK thermal characteristics were investigated by using a DSCTM200 Differential Scanning Calorimeter (DSC). A thermal ramp of 10°C/min starting from 40°C up to 360°C was applied. The DSC of the PEEK in the as-received state is reported in Fig. 1: it shows two endothermic melting peaks: the first one at lower temperature is related to the annealing process, whereas the other one at higher temperature is related to the melting point of the polymer [7]. The annealing treatment partially transforms the amorphous phase into a crystalline one

and helps in removing defects caused by machining after the polymer extrusion. The growth of new crystals that occurs during the heat treatment is witnessed by the formation of two additional melting peaks visible just before the melting point (T_m) at 344°C. The DSC analysis gives indication also for the glass transition temperature (T_g) at 154°C.

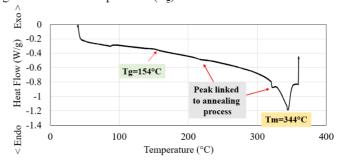


Fig. 1. DSC curve for PEEK in the as-received state.

2.2. Machining trials

The machining trials were carried out by using a Mori SeikiTM NL 1500 CNC lathe. The turning operations were performed with VCEX 110301L-F 1125 left-hand tool insert provided by Sandvik CoromantTM characterized by a rake angle (α) of 5°30' and corner radius (R) of 0.1 mm. Preliminary tests with inserts of different α values, namely 5°30', 6°, 10°, were conducted, since α is considered one of the crucial parameters in determining the surface roughness of polymers [8]. Nevertheless, the machined surfaces obtained with higher α values did not give satisfactory results, being characterized by higher surface roughness and amounts of defects compared to those surfaces obtained using inserts with α equal to 5°30'. The other cutting parameters were chosen according to the material manufacturer's guidelines for finishing turning of PEEK, prescribing feed (f) between 0.1 mm and 0.45 mm and cutting speed (V_c) between 200 m/min and 500 m/min.

The machining trials comprised two steps: first, the bar was roughened in order to achieve a diameter of 40 mm by using depth of cut (a_p) of 0.25 mm, feed of 0.1 mm/rev, and cutting speed of 200 m/min. Afterwards, a single finishing pass was performed to reach a final diameter of 39.5 mm by using an a_p of 0.25 mm and a length of cut of 5 mm. The other cutting parameters were changed according to the experimental plan reported in Table 1.

The machining tests were carried out under both dry and cryogenic conditions. The first machining strategy is mandatory to machine biomedical grade materials, since it avoids the contamination of the surface by metalworking fluids. To this reason, cryogenic machining is chosen as an alternative approach.

Table 1. Experimental plan for the machining trials.

ap (mm)	Vc (m/min)	f (mm/rev)	Machining condition
0.25	200	0.1	Dry/Cryo
0.25	300	0.1	Dry/Cryo
0.25	400	0.1	Dry/Cryo
0.25	200	0.01	Dry/Cryo
0.25	300	0.01	Dry/Cryo
0.25	400	0.01	Dry/Cryo

Indeed, cryogenic machining leaves the surface completely clean as in the case of dry cutting. In the present work, liquid nitrogen, stored at 15 bars in a Dewar, was sprayed simultaneously on the tool flank and rake faces by means of two copper nozzles of 0.9 mm of diameters. According to previous calculations by the Authors [6], the mass rate settles to 0.058 kg/s, while the heat exchanged by the system with the environment to 24.7 kW. During machining, the tool temperature was recorded by using a k-type thermocouple placed on a hole inside the cutting tool. A hole of 0.6 mm of diameter was drilled in the tool by electro-discharge machining 1 mm far from the cutting edge. The temperature recordings were collected and processed with a LabVIEWTM based software.

2.3 Surface integrity characterization

The machined surface finish was evaluated by using the Sensofar PLu NeoxTM optical profiler with a 20x magnification NikonTM confocal objective. The following areal surface parameters were assessed according to the ISO25178-2:2012 standard [9] after form removal.

- Sa, which represents the most commonly used parameter to evaluate the surface roughness;
- Spk, which represents the measure of the mean height of the peaks above the surface core roughness;
- Svk, which represents the mean valleys depth below the core roughness.

Additionally, the machined samples were inspected using a FEITM QUANTA 450 Scanning Electron Microscope (SEM) with the Secondary Electron (SE) probe, with a magnification of 500X and 800X to evaluate the presence of possible surface defects. In order to conduct the SEM inspection, the samples were gold-coated to make them conductive using a Denton VacuumTM Desk V machine, with a current of 25 mA for 240 s.

Each machined sample was also examined using the DSC with the same procedure described in §2.1. The percentage of crystallinity (Xc) was estimated from the heating scan of the DSC analysis considering the following equation:

$$Xc = \left(\frac{\Delta Hm}{\Delta Hm^{\circ}}\right) *100 \tag{1}$$

where $\Delta H \mathrm{m}^{\circ}$ is the melt enthalpy of the ideal 100% crystalline PEEK (equal to 130 J*g⁻¹), and $\Delta H \mathrm{m}$ the melt enthalpy determined from the DSC heating scan.

2.3 Tensile tests

To evaluate the PEEK mechanical characteristics at varying temperature, tensile tests were carried out at different temperatures, including those below zero.

Tensile tests on PEEK dog-bone samples were performed using an MTSTM-322 hydraulic dynamometer, equipped with the MTS-651TM environmental chamber. To perform elastic modulus measurements, a 632.53F-11 MTSTM extensometer was used. The testing temperature was varied in the range between -80 (±2) °C and 50 (±2) °C. This temperature range was chosen to reproduce the thermal field experienced by the

polymer during cutting. The strain rate (5 mm/min) and specimen size were designated in accordance to [10]. More details about the equipment and testing procedures are given in [11].

3. Results

3.1 Surface finish of the machined samples

SEM images of the surface morphology of the samples machined at f=0.1 mm/rev are reported in Fig. 2. In dry condition, prominent feed marks and flakes were left on the surface by the machining process. The cutting speed increase boosted the deterioration of the surface since much more flakes appeared. By applying liquid nitrogen as a coolant, a reduction of the surface defects was visible, regardless of the cutting speed. As a matter of fact, less residual flakes as well as less marked feed marks were detectable.

A different scenario was obtained in the case of f=0.01 mm/rev, whose SEM images are reported in Fig. 3. Under dry condition the surfaces were homogeneous, with minimal residual flakes; nevertheless, a lot of grooves aligned parallel to the feed marks direction appeared at higher Vc.

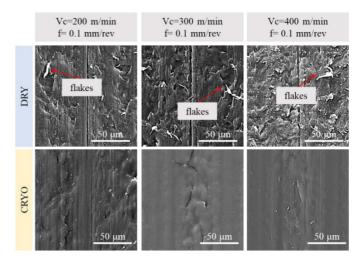


Fig. 2. SEM images of the machined surfaces as a function of the cutting speed and machining condition (*f*=0.1 mm/rev).

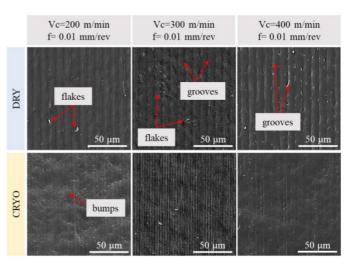


Fig. 3. SEM images of the machined surfaces as a function of the cutting speed and machining condition (f=0.01 mm/rev).

Contrarily to what found for the highest feed, the cutting speed increase contributed to enhance the surface finish. In the case of cryogenic cooling, the flakes disappeared, even if several parabolic-shape features were left on the surface, especially at the lowest cutting speed. Nevertheless, even in this case, the cutting speed increase led to an improvement of the surface finish.

The above reported qualitative SEM observations were confirmed by the surface roughness data plotted in Fig. 4. At the highest feed, under dry conditions, the surface roughness worsened at increasing cutting speed.

Contrarily, in the case of cryogenic turning and at the highest feed, the surface roughness improved by changing the cutting speed from 200 m/min to 300 m/min, and afterwards it tended to stabilize. At the highest feed, the surface roughness decreased of 13%, 33% and 29% for cutting speed equal to 200 m/min, 300 m/min and 400 m/min, respectively.

On the contrary, at the lowest feed, a clear trend cannot be identified. As example, compared to the dry case, cryogenic machining led to 83% increment of surface roughness at V_c =300 m/min, whereas a 27% reduction was found for V_c =400 m/min.

Overall, cryogenic machining represents the optimal condition at the highest feed, whereas dry cutting at the lowest one.

The Spk/Svk ratio was chosen as an indicator of the machining quality according to [12]. A low Spk/Svk ratio means that there are more deep valleys than high peaks, which can be helpful in decreasing the formation of wear particles that arise from the contact between mating surfaces. This can be beneficial for biomedical applications, since it can contribute to reduce the wear rate as well as possible immune system responses in the patient. Except for the lowest cutting speed, the use of cryogenic machining led to the Spk/Svk reduction. The effect of the cutting speed was dependent on the applied machining conditions. Actually, in the dry case, the cutting speed increase led to the Spk/Svk increase, regardless of the feed.

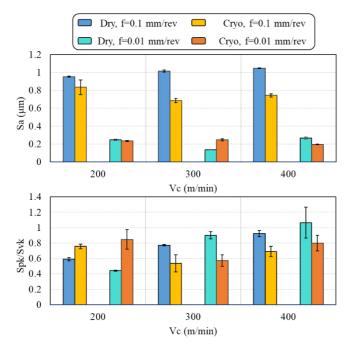


Fig. 4. Sa and Spk/Svk as a function of the cutting conditions.

In the case of cryogenic conditions, the lower the cutting speed the higher the Spk/Svk. In general, the lower the feed the lower the defects formation, since Spk/Svk at the lowest feed was lower compared to its counterpart obtained at the highest feed.

3.2 Surface integrity of the machined samples

Fig. 5 reports the DSC scans of the samples machined at V_c = 300 m/min and f= 0.1 mm/rev in dry and cryogenic conditions. From the Figure, it can be seen a slight increase of the melting peak area in the case of cryogenic conditions. It is worth underlining that for the dry case the small exothermic peak, which is located at the same temperature as the one of the asdelivered condition (see Fig. 1), was included in the calculation.

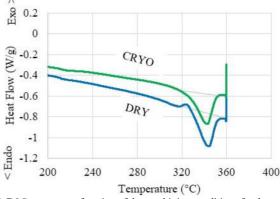


Fig. 5. DSC curves as a function of the machining conditions for the samples machined at V=300 m/min and f=0.1 mm/rev.

Table 2 reports the *Tm*, *Tg*, *Hm* and *Xc* values, derived from the first heating cycle of the DSC scan, for the samples machined at f= 0.1 mm/rev. It can be seen that both the *Tm* and *Tg* were not affected by machining, being unaltered compared to the values of the as-received material. The melting enthalpy, namely the degree of crystallinity, was, instead, slightly affected by the applied machining conditions. The degree of crystallinity was higher in the samples machined under cryogenic conditions, namely the cryogenic machining allowed the formation of less amorphous surfaces. PEEK crystals consist of very fine lamellae that under certain conditions can organize into larger spherulites, according to [13]. As the temperature reached during cryogenic turning was much lower than the one in the dry condition, it led to less breakage of the crystalline domains.

Fig. 7 shows the SHORE D hardness in correspondence of the surface of the machined samples at different feeds.

Table 2. T_m , E_m and ΔX_c obtained from the DSC heating scans (f=0.1 mm/rev).

Vc (m/min)	Machining conditions	Tm (°C)	Tg (°C)	Hm (W/g)	Xc (%)
200	Dry	344	153	30	23
300	Dry	343	154	29	22
400	Dry	343	157	28	21
200	Cryo	344	157	34	26
300	Cryo	341	156	32	24
400	Cryo	344	155	33	26

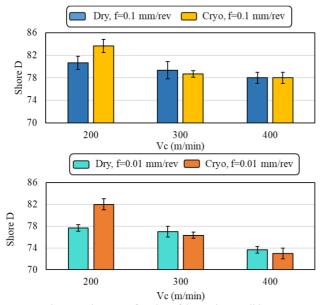


Fig.6. Hardness as a function of the cutting conditions

Solely at the lowest cutting speed, the cryogenic machining contributed to increase the hardness of the surface. This can be due to the increased degree of crystallinity, which positively affects the material mechanical strength [14].

4. Discussion

The knowledge of the temperature reached during machining is of primarily importance when cutting polymers, because it significantly influences their mechanical behavior. In general, either higher cutting speed or cooling-assisted processes are employed to machine polymers to limit the temperature increase so as to carry out the cutting process within the glassy regime [15]. In the case of PEEK, the glass transition temperature is 154°C, namely the polymer is stiff enough to be machined. Nevertheless, frictional heating during the machining process can cause inhomogeneous plastic deformation leading to poor surface finish, as proved by the results shown in Figs. 3 and 4.

Fig. 7 shows the tool temperature, as measured through the tool thermocouple when machining at f=0.1 mm/rev. It is worth underlining that the tool temperature was assumed as indicative of the one of the workpiece. Whilst in dry conditions temperatures arrived above 60° C at the highest cutting speed, in the case of cryogenic conditions they fell down significantly below zero.

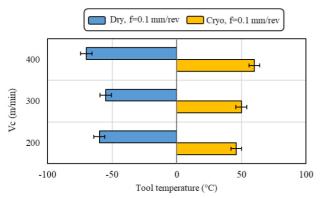


Fig.7. Cutting temperature as a function of the cutting conditions

Results are displayed in Fig. 8, whereas Table 3 summarizes the data derived from the engineering stress curves.

The shape of all the tensile stress-strain curves is similar, comprising four stages, underlined for sake of clarity for the tensile curve at the highest temperature in Fig. 8: elastic stage (I), uniform deformation stage (Π), diffusion necking stage (III), and localized necking stage (IV) [16]. During stage I, the stress rises monotonically at increasing strain. Afterwards, in stage II, work hardening dominates, leading to the formation of necking due to the onset and growth of micro-voids and microcracks within the material. Due to the material strain-rate sensitivity, the deformation resistance in the necking area increases, and the local deformation decreases. Then, the necking transfers to the sections with relatively weak deformation resistance, spreading continuously, and requiring less force to deform the specimen (stage III). With further straining, the damage inside the specimen becomes more and more serious, which results that the necking diffusion cannot continue anymore. Finally, during stage IV, localized necking takes place inducing a rapid drop of the flow stress.

As shown in Fig. 8, the length of stage III substantially decreased as the testing temperature was reduced. A similar behavior is obtained at increasing strain rate [16]. This is because low strain rate provides longer time for energy accumulation inside the polymer. This reflects in a different material response during cutting. As shown in Fig. 3 for the highest feed, in dry condition, the machined surfaces are characterized by high quantity of flakes, which are residues of fibrils, which were detached, stretched in a ductile way, and finally broken. On the contrary, under cryogenic conditions, the deformation ability of the fibrils was suppressed, contributing to form almost defects free surfaces. The situation was further improved at the highest cutting speed because of the hardening behaviour at elevated strain rate, which is typical of polymers.

A different scenario can be seen in the case of the lowest feed. In fact, whilst dry cutting was carried out still in the ductile region, in the case of cryogenic conditions the experiments were carried out almost in the brittle regime. The amounts of surface defects directly influence the surface roughness values as demonstrated by the results of Figs. 4 and 5.

Fig. 8 shows that, thanks to cutting at low temperature, besides decreasing the strain at rupture, stiffer surfaces were gained.

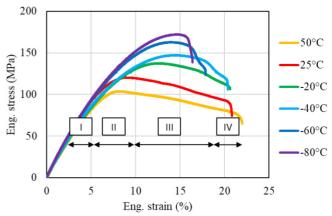


Fig. 8. Engineering stress curves at different temperatures.

As example, the elastic modulus (E) increased up to 15% from 25°C to -60 °C. This had an impact on the machined surface integrity in terms of hardness and crystallinity degree.

Increasing the temperature increases the vibrational, rotational, and translational motions in a polymer, thus decreasing the time it takes to respond to a disturbance in a given manner [17]. In other words, the relaxation time decreases with increasing temperature. This means that the rupture of spherulites is easier when deformed in dry conditions, leading to the formation of softer surfaces.

Table 3. PEEK mechanical characteristics.

T (°C)	E (GPa)	ε _r (%)	σу (MPa)
50	4.0	22.0	103
25	4.1	20.8	120
-20	4.3	20.6	137
-40	4.5	20.4	147
-60	4.7	18.0	163
-80	4.9	16.4	172

5. Conclusions

In the present paper, cryogenic machining was evaluated as an alternative to dry machining of biomedical grade PEEK. To this purpose, turning trials at varying cutting speed and feed were performed. Additionally, tensile tests were carried out in the different temperature regimes for the PEEK.

The following conclusions can be drawn:

- At f=0.1 mm/rev, cryogenic machining led to the formation of lower amount of defects compared to the corresponding dry case, favoring a sensible surface roughness reduction, regardless of the adopted cutting speed. The cutting speed increase deteriorated the dry machined surfaces, whereas the opposite was obtained under cryogenic conditions.
- At f=0.01 mm/rev, flakes and grooves were left on the dry machined surfaces, whereas parabolic shape features were visible in the case of cryogenic cooling. A clear effect of the cutting speed on the surface roughness was not found under both the machining conditions.
- Except in the case of the lowest cutting speed, cryogenic machining always led to the reduction of the Spk/Svk ratio.
- A slight crystallinity increase was promoted by the cryogenic machining.
- Cryogenic machining promoted the formation of harder surfaces at the lowest cutting speed.
- Mechanical tensile tests confirmed a lower deformation capability of PEEK at temperatures

- below the room one, which justifies the reduction of the flakes amount when cutting was carried out in cryogenic conditions.
- Stiffer surfaces were obtained as the temperature was reduced, thus favoring the preservation of hardness and increase of crystallinity.

On the basis of the experimental findings, the use of cryogenic machining can be suggested in finishing cutting biomedical grade PEEK since it allows productivity increase thanks to the adoption of higher feed and cutting speed than dry cutting, besides assuring an enhanced surface integrity of the machined surfaces.

Future studies will be devoted to the investigation of the machined PEEK wear resistance under in-vitro conditions.

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