Laser Surface Modification of Poly(etheretherketone) to Enhance Surface Free Energy, Wettability and Adhesion

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Abstract

Enhancement of the surface wettability and surface free energy of thermoplastic materials is an effective way of improving their adhesion and consequently the adhesive joint strength. A nanosecond pulsed Nd:YAG laser was selected in this work to provide energetic treatment of PEEK surfaces, in order to investigate its effectiveness in increasing the performance of lap shear adhesive joints. The laser was used to irradiate the PEEK, by rastering a spot of ca. 1 mm diameter across a large area. The resulting surfaces were characterised using single lap shear testing, confocal laser scanning microscopy, contact angle analysis, FT-IR, XPS and ToF-SIMS. Single lap shear testing of PEEK joints showed that the strength of adhesively bonded joints is greatly improved by laser treatment, up to 13 times that of untreated PEEK. Confocal laser scanning microscopy showed that the higher laser powers intensities ($\geq 10^7 \text{ W mm}^{-2}$) disrupted the surface of the PEEK more than the lower laser powers intensities ($< 10^7 \text{ W mm}^{-2}$), but also showed that, as expected, only some of the surface is treated by the laser. Contact angle analysis showed a decrease in water contact angle with increasing laser power intensity, and the derived surface free energy increased accordingly. FT-IR in the specular reflectance

mode showed no discernible change but XPS and ToF-SIMS did, suggesting that laser treatment only affects the near surface at the extremity of the 1-2 μm sampling depth. XPS showed a decrease in the carbon/oxygen ratio of PEEK on treatment, indicating that oxygen-containing functional groups were being created at the surface. XPS also suggested a cleaning mechanism at a laser intensity of 7.83×10^6 W mm^{-2} , progressing to surface modification from a laser intensity of 10^7 W mm^{-2} and above. ToF-SIMS confirmed that laser treatment cleans the surface of PEEK of extraneous material.

Introduction

Poly(etheretherketone) (PEEK) is increasingly being used in long and short term implantable medical devices such as cranial implants, hip implants and replacement heart valves. It is being used as an alternative to traditional materials such as titanium and ceramics and also to create new device platforms, surgical approaches and techniques. These can be realised completely with polymers or in combination with traditional biomaterials. Selection and application of an appropriate surface treatment is one of the major factors in achieving good wettability and improving long term durability in bonded joints, whereas inadequate surface treatment is one of the most common causes of joint failure. For polymers with low surface free energy such as PEEK, it is advantageous to introduce chemically reactive surface functional groups in order to improve adhesion.

Energetic treatments such as plasma or corona discharge have been used on polymer materials with good levels of success (1-10); however laser treatment gives the potential to target specific areas, and to provide different treatments in different positions of a device with greater precision than alternative techniques. Laser treatment has been used in the past to functionalise the surfaces of several low-energy polymers to enhance their usability in multiple applications (11-13). There are several types of lasers which can be utilised, such as excimer, Nd:YAG and diode lasers . (14-17).

This paper reports the effects of laser surface treatment of PEEK with a nanosecond pulsed Nd:YAG laser in the near infrared region, at different laser power intensities. First, the joint strengths of adhesively bonded laser treated PEEK was investigated to determine whether the effect was positive. The laser treated surfaces were characterised to determine the changes in surface free energy, and then the changes in the chemical composition of the PEEK surfaces were studied.

Materials and Methods

PEEK material

The PEEK used was unfilled injection moulded PEEK, with a thickness of 3.92 mm. Isopropyl alcohol was used to degrease the surfaces of all samples prior to laser treatment and testing. A medical grade cyanoacrylate adhesive (Loctite 4061) was used to bond the PEEK lap shear joints.

Laser surface treatment

A nanosecond pulsed q-switched Nd:YAG laser with an output wavelength of 1064 nm was used. The pulse energy was calibrated using an Ophir 10A-P-SH energy meter, and the spot size using photosensitive paper.

The position of the sample plaque (12.5 mm x 25 mm) under the laser was controlled using a computer numerical controlled (CNC) two-axis table. The table was set to move horizontally backwards and forwards underneath the laser aperture, in both the x and y direction to provide parallel tracks, or rows, of treatment. Movement was achieved between laser pulses so that the laser treated region received a definitive number of shots, each well separated from the others. This was done to avoid a variable dose that would result from continuous rastering of the table, with movement occurring during both the on and off parts of the laser duty cycle. The treated area was ca. 12.5 x 25 mm². A schematic of the setup is given in Figure 1. Some preliminary work was performed with a broad range of laser power intensities to identify a suitable range for investigation. This was determined via single lap shear testing, a common adhesive joint geometry, to be around 1.0 x10⁷ W mm⁻². Further work was then performed in a range proximal to this value, as described in Table 1.

Equation 1 was used to convert spot size and laser energy into power intensity:

$$J = E / (t.a) \dots\dots \text{Equation 1}$$

Where:

J = Power intensity (W mm⁻²), **E** = Pulse energy (J), **t** = Pulse duration (s) and **a** = laser treatment spot area (mm²).

Mechanical testing

The first investigation was to determine the effect of the laser pre-treatment on the adhesive joint strength of the PEEK and if there were any obvious changes in the locus of failure.

Lap shear tests were performed on PEEK-to-PEEK bonded joints. These were fabricated using PEEK coupons of 50 mm x 25 mm x 3.92 mm dimensions, adhesively bonded using Henkel Loctite 4061, with an overlap area of 12.5 mm x 25 mm and a bond line thickness of 0.1 mm controlled with glass ballotini. Specimens were tested in shear using a Hounsfield Universal Testing Machine at a crosshead speed of 1.3 mm min⁻¹, as per ASTM D-1002. Three samples per treatment level were tested. The test coupons were fabricated shortly after the laser treatment of the PEEK and were tested the following day after storage in aluminium foil.

The lap-shear data, collated in Table 2 and depicted in Figure 2, confirms that the laser surface treatment positively affects the adhesion of bonded PEEK joints. Depending on the intensity of the laser power selected, the joint strength increased by a factor of 2-13 following laser surface treatment in air. There is a sharp increase in strength at a power density of 10⁷ W mm⁻². Visual assessment of the locus of failure of the adhesive joints shows that a change occurs at this critical value from interfacial failure at lower laser power intensity to cohesive within the PEEK or the adhesive at higher laser power intensities. This observation, along with the increased strength values, indicated that the laser treatment is improving the adhesion between the PEEK and the adhesive, although it was not clear whether this is a result of chemical modification of the surface or the removal of a weak boundary layer which may have been present due to the migration of processing aids to the surface. A detailed surface examination was conducted to further clarify the reasons for this positive outcome.

Surface characterisation

Surface characterisation techniques were used to investigate both the untreated and treated PEEK surfaces. Confocal laser scanning microscopy (CLSM) was carried out using an Olympus LEXT OLS4000 microscope to examine the

topographical changes brought about by the laser treatment. Contact angle analysis was performed using a Krüss DSA100, using the sessile drop method. Deionised water and diiodomethane were used as the test liquids, and the drop volume was 5 µl. Droplets were placed over the treated areas. Surface free energy calculations were performed using the Owens, Wendt and Kaelble method (18, 19), within the Krüss software. The values for the surface tension of water and diiodomethane used in the measurements and their respective dispersive and non-dispersive (hydrogen bonding) components are provided in Table 3. Chemical analysis was carried out by Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). FT-IR was carried out using an Agilent Exoscan 4100 in the specular reflectance mode. Spectra were acquired in the range 1 – 3250 cm⁻¹. XPS analysis was carried out using a Thermo Scientific Theta Probe with a monochromated AlK α source and a spot radius of 400µm. The spot was positioned in the centre of the treated regions to ensure that the area analysed had been wholly laser treated. A pass energy of 100 eV was used to obtain survey spectra, a pass energy of 20 eV was used to obtain high resolution spectra, and an electron/ion flood gun was used for charge compensation. Peak fitting was performed using Thermo Scientific *Avantage* v.5.9 software. A TOF.SIMS 5 system (ION-TOF GmbH Münster Germany) was used to investigate the top few nanometres of the treated PEEK surface and to provide molecular information about the elements already recorded using XPS. Static SIMS conditions of $<1 \times 10^{13}$ ions cm⁻² were employed using a Bi₃⁺ primary ion beam in the high current bunched mode of operation. This was rastered over a 100 x 100 µm² area. Positive and negative spectra were acquired in the range 1-330 mass units (u).

As the laser spot size was in the range 0.6 - 2.6 mm diameter depending on laser power (see Table 1), care was taken to ensure that the analytical data was taken from within the treated zone.

Results

Surface topography

CLSM images of PEEK specimens treated at 2 different laser power intensities were recorded. First, an overall view of the surface was recorded, as shown in

Figure 3 for a treatment intensity of $7.83 \times 10^6 \text{ W mm}^{-2}$ (spot diameter 1.1 mm) and Figure 5 for $2.78 \times 10^7 \text{ W mm}^{-2}$, (spot diameter 0.6 mm) followed by images of single spot features which were created by the laser treatment. 3D images of the respective treatments are given in Figure 4 and Figure 6.

Figure 5 shows an overall image of the surface of the PEEK specimen treated at $2.78 \times 10^7 \text{ W mm}^{-2}$. From this first observation the laser treated areas are shown as discrete spots on the surface. The spots, as shown in Figure 6, are around $20 \mu\text{m}$ deeper than at $7.83 \times 10^6 \text{ W mm}^{-2}$. The laser treatment also quite clearly covers only a small proportion of the total surface area of the PEEK. It is estimated that the sample treated with a laser power intensity of $7.83 \times 10^6 \text{ W mm}^{-2}$ has around 4-5% treated of the total sample area, and the sample treated with a laser power intensity of $2.78 \times 10^7 \text{ W mm}^{-2}$ has around a 20% treated area. It would be reasonable to suggest that with a greater percentage of treated area, the enhancement of joint strength would be increased further, which could be easily achieved by modification of the CNC table parameters.

Surface free energy

The contact angles (θ) were recorded a day after treatment as indicated in Table 4. Dispersive (γ^D) and polar (γ^P) contributions to the total surface free energy (γ^T), and the mean contact angle for each parameter are displayed.

The surface free energy calculations in Table 4 show a sharp increase in total surface free energy at a laser power intensity exceeding 10^7 W mm^{-2} . This is shown by an increase in polar energy, and is characterised by a sharp decrease in water contact angle.

The surface free energy calculations indicated that it was possible to increase the surface free energy significantly and improve the wettability. A laser power intensity of 10^7 W mm^{-2} appears to be the point at which surface changes occur. This could be due to formation of functional groups. Further analytical characterisation was performed to confirm this.

Chemical composition of the PEEK surface

The chemical nature of the PEEK surface before and after laser treatment was investigated using FT-IR spectroscopy. The spectra for the control sample and the most intense PEEK treatment levels are shown for comparison in Figure 7,

with peak assignments provided in Table 5. The FT-IR analysis was performed on samples processed at all laser intensities, but only the significant data is presented. The wavenumber values are shown both spectra and are identified by reference to the absorbance bands of Table 5. The FT-IR measurements do not show any significant change between the untreated and treated specimens, possibly due to the 1-2 μm sampling depth of the technique. This was considered a useful result, as it suggests that whatever changes are occurring, they might be occurring closer to the surface of the PEEK than FT-IR can detect, and therefore the effects are exclusively surface effects. XPS and ToF-SIMS were employed next to further investigate the top few nanometres of the PEEK surfaces.

The XPS analysis of PEEK specimens above and below the critical 10^7 W mm^{-2} value of laser treatment shows a number of changes to the surface composition. The surface composition, by XPS, for all samples investigated is presented in Table 6. A number of observations can be made. Firstly, the carbon: oxygen elemental ratio decreased with increased laser intensity. Comparing the survey spectrum of the untreated PEEK in Figure 8 with that of the laser treated PEEK in Figure 9 this effect is clearly seen in the change in relative intensities of the C1s (285 eV) and O1s (532 eV) peaks. Secondly, the proportion of nitrogen, silicon, sodium, chlorine and sulphur changes with different laser power intensities. The proportion of nitrogen on the surface increases slightly with increasing laser intensity. This would suggest either nitrogen combining with oxygen and forming on the surface, or combining with carbon to form amine groups, as reported by Kinloch *et al* (18). The amount of silicon on the surface increases after laser treatment, which was found to be polydimethylsiloxane (PDMS) once ToF-SIMS analysis was completed. The amount of sodium decreased at a laser intensity of $7.83 \times 10^6 \text{ W mm}^{-2}$. It is suggested that the surface is cleaned of extraneous sodium-based contamination, most likely in the form of sodium chloride because the proportion of chlorine decreased also. This would indicate that such contamination is a result of uncontrolled handling at some point in the history of the PEEK stock. The source of the very low concentration of zinc observed in the XPS survey spectrum of Figure 8 ($\text{Zn } 2p_{3/2} = 1021 \text{ eV}$) is not clear but is assumed to be associated with an organo-zinc processing aid. As indicated in Figure 9 this trace amount is readily removed by laser treatment. The proportion of sulphur on

the surface following laser treatment is reduced to zero, suggesting removal of sulphur-based contamination such as SO, SO₂ and SO₃. Finally, the environment of the carbon atoms on the surface of the PEEK changes after laser treatment. Further information to support the increase in the proportion of oxygen can be found by examining the high resolution spectrum of carbon. Peaks in the high resolution XPS C1s spectra of virgin PEEK in Figure 10, are consistent with non-bonded aromatic carbon at 285.0 eV, aromatic carbon bonded to oxygen (C-O) at 286.7 eV and carbonyl (C=O) at 288.0 eV, which are all found within the structure of PEEK. At a laser power intensity of $7.83 \times 10^6 \text{ W mm}^{-2}$, shown in Figure 11, there is an increase in the hydroxyl (C-O) groups and a slight decrease in carbonyl (C=O) groups. There is also the appearance of a peak at 289.3 eV, characteristic of carboxylic acid (O-C=O) groups. The increase in O-C=O groups and the decrease in C=O groups suggests a replacement of the original C=O groups of the PEEK structure with new carboxylic acid groups. The mechanism that may be occurring is the forming of polar functional groups on the surface, as supported by the contact angle data and the XPS data. This is preceded by chain scission initiated by the energetic nature of the laser treatment and resulting in new polymer chain ends at the surface, terminated by carbonyl groups. This mechanism increases the proportion of oxygen on the PEEK surface, resulting in a higher surface free energy, and consequentially greater adhesion strength.

ToF-SIMS analysis showed some changes to the chemical composition of the PEEK surface due to laser treatment. Firstly, polydimethylsiloxane (PDMS) appears on the laser treated PEEK surface. This is characterised by the peaks at 43, 147, 221 and 281 in the positive ToF-SIMS spectrum of laser treated PEEK in Figure 13. Secondly, extraneous material is removed by the laser. Peaks in the negative spectrum in Figure 14, at 80, 183, 255, 265, 311 and 325, are reduced following laser treatment, shown in the negative SIMS spectrum of the treated PEEK in Figure 15.

In order to assess the source of the PDMS, a sample section of the bulk of the PEEK was cut from a coupon using a fresh scalpel blade, the ToF-SIMS spectra from this specimen are shown in Figure 16. The peaks at 43, 147, 221 and 281 of Figure 16 confirm that the bulk sample of PEEK contains PDMS, and therefore suggests that as a result of the laser treatment the PDMS has migrated to the

surface of the PEEK. The PDMS does not appear to have any detrimental effect on the lap shear strength of the laser treated PEEK, and this is supported by the work of Vickers *et al* (21). They found that the interlaminar strength of carbon fibre reinforced polymers, manufactured from pre-preg stock with PDMS surface contamination (from the protective peel plies) was not adversely affected by the presence of PDMS. They noted, however that addition of a PDMS of high molecular weight to pre-preg surface prior to composite manufacture did compromise performance. The interpretation was that low molecular weight material could readily diffuse away from the prior pre-preg interface, perhaps forming an interpenetrating network, whilst the more viscous material was much less mobile and formed the usual weak boundary layer.

Discussion

As described above, PEEK can be subjected to a laser surface treatment before adhesive bonding, and that the lap shear strength of the bonded joint is subsequently improved. The surface free energies of the PEEK specimens have been measured and the chemical compositions of the treated surfaces have also been studied.

The lap shear tests, contact angle measurements and surface chemical analyses can be quantitatively related. All methods of analysis show that at a laser power intensity of 10^7 W mm^{-2} and above a significant change to the PEEK surface is occurring. The surface free energy significantly increases at this laser power intensity and this will improve the extent of wetting of the cyanoacrylate adhesive onto the PEEK surface. As the dispersive part of the surface free energy remains relatively unchanged, and the polar contribution to surface free energy increases, it can be suggested that the PEEK-adhesive interfacial forces are enhanced via dipole-dipole, hydrogen bonds and other acid-base interactions. This is supported by the XPS analysis which shows formation of C-O, C=O and O-C=O functional groups on the treated PEEK surface and a decrease in the carbon; oxygen ratio.

The presence of weak boundary layers is a cause for concern in many adhesively bonded joints. The first type of weak boundary layer concerns weak surface regions of the substrate, as reported by Kinloch & Yuen (22). This phenomenon has not been evident during the laser treatment of PEEK studies, as laser

treatment moves the locus of failure completely to the substrate and not the joint's interface. The second type of weak boundary layer that Kinloch and Yuen mention is as a result of extraneous materials such as mould release agents and contaminants on the surface. It has been shown in this work that the untreated PEEK substrate does possess these extraneous materials on the surface, and that the laser treatment is successful at removing them to a certain degree. While the laser treatment has also been shown to promote PDMS to the surface of the PEEK. The locus of failure is still moved to the substrate, the surface free energy increases and the lap shear joint strength increases. It can therefore be suggested that weak boundary layers in this case are not detrimental to these particular adhesively bonded joints.

The laser treatment has changed the topography of the PEEK surface by introducing craters at the points of laser incidence. Kinloch *et al* (20) reported that surface topography of thermoplastic composites after corona treatment does not have a major effect on the adhesive joint properties, and a similar assumption can be made here. To support this theory, we can observe that the dispersive component of surface free energy does not change much after laser treatment, from 43.4 mJ m⁻² in the control sample to an average of 42.87 mJ m⁻² at a laser power intensity of 10⁷ W mm⁻². As a final consideration, the droplet sizes used during the contact angle measurements were larger than the feature sizes produced by the laser, meaning the droplets were not pinned by any topography. Surface features that are contained entirely within a droplet will not have an effect on the contact angle measurements, as reported by Gao & McCarthy (23). This means that the surface free energy measurements taken have not been skewed by the topography of the sample.

It has been shown that a specific laser power intensity of 10⁷ W mm⁻², at a wavelength of 1064 nm, can be defined as the threshold laser power intensity required to chemically change the surface of PEEK for improved adhesive bonding in medical applications, for example. This threshold laser power intensity may be applied to other laser sources and provide a method of surface treatment which is equally as effective, yet more accurate and localised than alternatives such as plasma or corona treatment.

Conclusions

Surface treatment of PEEK using an Nd:YAG laser has led to the following conclusions:

- Laser treatment of PEEK increased the lap shear strength of adhesively bonded joints by up to a factor of 13.
- The locus of failure for the untreated as compared with the treated PEEK to PEEK bonded joint moved from interfacial to cohesive within the substrate.
- Surface topographical changes were introduced by the laser treatment but it cannot be determined with certainty whether they contribute to the improvement in surface free energy or adhesion properties.
- Laser treatment of PEEK increased the surface free energy from 44.9 mJ m^{-2} to 72.5 mJ m^{-2} , mainly via an increase in the polar component.
- Chemical changes on the PEEK surface were not easily detectable using FT-IR, but were identified by XPS and ToF-SIMS, suggesting that changes are made on the top 1-10 nm of the material.
- XPS of PEEK showed a reduction in carbon/oxygen ratio with increasing laser intensity on PEEK.
- Functional groups in the form of carbonyls and carboxylic acid groups formed on the PEEK surface.
- ToF-SIMS indicated that laser treatment removed extraneous material from the surface of the PEEK, and recorded an increase in PDMS on the surface. This was deemed to be PDMS from the bulk which had migrated to the surface.

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Table 1 - PEEK treatment procedures, at a pulse duration of 10 ns, pulse repetition rate of 10 Hz, linear stage speed of 12 mm s⁻¹ and a pulse energy of 78.5 mJ.

Sample	Spot diam. mm	Power intensity W mm ⁻²
PEEK A	2.5	1.65x10 ⁶
PEEK B	2.0	2.58x10 ⁶
PEEK C	1.6	4.11x10 ⁶
PEEK D	1.1	7.83x10 ⁶
PEEK E	1.0	9.99x10 ⁶
PEEK F	0.9	1.23x10 ⁷
PEEK G	0.6	2.78 x10 ⁷

Table 2 - Tensile shear tests one day after laser treatment on samples with 25 mm x 12.5 mm overlap.

Sample	Intensity (W mm ⁻²)	Max load (N)	Mean max load (N)	Standard error	Failure mode
Control	Control	150	136.3	5.6	B
		129			B
		130			B
PEEK A	1.65x10 ⁶	458.5	262.8	85.6	B
		229.9			B
		100			B
PEEK B	2.58x10 ⁶	543.2	484.4	28.0	B
		424.3			B
		485.7			B
PEEK C	4.11x10 ⁶	459.8	663.6	108.9	B
		914.5			B
		616.5			B
PEEK D	7.83x10 ⁶	857.7	811.5	64.5	B+C
		657.5			B+C
		919.4			B+C
PEEK E	9.99x10 ⁶	1710	1888.0	72.7	A+B+C
		1982			A
		1972			A
PEEK F	1.23x10 ⁷	1374	1425.3	34.3	A
		1508			A
		1394			A
PEEK G	2.78x10 ⁷	1048	1310.0	107.5	B+C
		1463			A
		1419			B+C

Note: The failure mechanisms are: A – Cohesive failure of the PEEK substrate, B - Interfacial failure between adhesive and parent, C - Cohesive failure of the adhesive

Table 3 - Surface tension values for water and diiodomethane used in surface free energy calculations as per the Owens, Wendt and Kaelble (18,19) method.

Liquid	Surface tension (mN m ⁻¹)	Dispersive Contribution (mN m ⁻¹)	Non-dispersive Contribution (mN m ⁻¹)
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	0

Table 4 - PEEK surface free energy one day after treatment.

Sample	Power intensity (W mm ⁻²)	Contact angle		Surface free energy			
		Mean θ_{water} (°)	Mean θ_{dm} (°)	γ^D (mJ m ⁻²)	γ^P (mJ m ⁻²)	γ^T (mJ m ⁻²)	Mean γ^T (mJ m ⁻²)
Control	N/A	85	32	43.4	1.4	44.9	44.9
PEEKAs1	1.65x10 ⁶	84	40	37.5	1.5	39.0	42.0
PEEKAs2				41.4	3.3	44.7	
PEEKAs3				40.2	2.0	42.2	
PEEKBs1	2.58x10 ⁶	79	46	38.0	4.8	42.8	40.9
PEEKBs2				35.1	3.7	38.8	
PEEKBs3				35.5	5.7	41.1	
PEEKCs1	4.11x10 ⁶	90	40	41.1	0.4	41.5	40.8
PEEKCs2				36.8	2.1	38.9	
PEEKCs3				41.4	0.7	42.1	
PEEKDs1	7.83x10 ⁶	86	44	41.6	3.3	44.9	39.9
PEEKDs2				35.0	1.9	36.9	
PEEKDs3				36.3	1.6	37.9	
PEEKEs1	9.99x10 ⁶	35	33	43.4	23.2	66.6	67.9
PEEKEs2				42.7	22.3	65.0	
PEEKEs3				42.5	29.5	72.0	
PEEKFs1	1.23x10 ⁷	25	32	39.3	28.9	68.2	72.5
PEEKFs2				45.5	28.2	73.7	
PEEKFs3				45.0	30.7	75.7	
PEEKGs1	2.78x10 ⁷	72	28	43.3	6.3	49.6	50.5
PEEKGs2				45.9	3.2	49.1	
PEEKGs3				45.9	7.0	52.9	

Table 5 - Assignments of FT-IR peaks of PEEK material.

PEEK
Wavenumber (cm ⁻¹)	Assignment	
1648	C=O stretch in ketone	
1601	Skeletal in-plane vibration of aromatic ring	
1492	Skeletal semi-circle stretch of aromatic ring	
1412	Aromatic rotations	
1311	Aromatic rotations	
1286	Aromatic rotations	
1227	Diphenyl ether group, C-O-C rotation	
1190	Diphenyl ether group, C-O-C stretch	
1163	Diphenyl ether group, C-O-C stretch	
1115	C-O stretch	
1012	In-plane vibrations of aromatic hydrogens	
948	Aromatic out-of-plane bending	

Table 6 Surface composition of PEEK surfaces after selected laser treatment intensities, obtained using XPS.

	C1s	O1s	N1s	Na1s	S2p	Si2p	Cl2p	C/O ratio
Control	78.26	16.05	2.05	1.39	1.04	0.88	0.34	4.9
7.83 x 10 ⁶ W mm ⁻²	74.89	21.1	1.22	0.55		2.03	0.21	3.6
2.78 x 10 ⁷ W mm ⁻²	72.52	21.6	2.36	2.17	0.04	1.03	0.28	3.4

Figure 1 - Schematic diagram of laser treatment setup

Figure 2 - Tensile shear tests on PEEK with 25x12.5mm overlap showing standard error of results.

Figure 3 - CLSM image taken of surface of PEEK sample at $7.83 \times 10^6 \text{ W mm}^{-2}$ laser power intensity, showing multiple laser treated spots.

Figure 4 - CLSM 3D colour coded image of one laser treated spot on PEEK surface at $7.83 \times 10^6 \text{ W mm}^{-2}$ laser power intensity. The scale is in μm .

Figure 5 - CLSM image taken of surface of PEEK sample at $2.78 \times 10^7 \text{ W mm}^{-2}$ laser power intensity, showing multiple laser treated spots.

Figure 6 - CLSM 3D colour coded image of one laser treated spot on PEEK surface at $2.78 \times 10^7 \text{ W mm}^{-2}$ laser power intensity. The scale is in μm .

Figure 7 - Selected FT-IR spectra of control sample (top) and laser intensity $2.78 \times 10^7 \text{ W mm}^{-2}$ (bottom) for PEEK.

Figure 8- XPS survey spectrum of untreated virgin PEEK material.

Figure 9 - XPS survey spectrum of laser treated PEEK material at a power intensity of $2.78 \times 10^7 \text{ W mm}^{-2}$.

Figure 10 - High resolution C1s XPS spectrum of untreated PEEK.

Figure 11 - High resolution C1s XPS spectrum of PEEK treated at $7.83 \times 10^6 \text{ W mm}^{-2}$.

Figure 12 - Positive ToF-SIMS spectrum of untreated PEEK specimen.

Figure 13- Positive ToF-SIMS spectrum of PEEK treated at $9.99 \times 10^6 \text{ W mm}^{-2}$.

Figure 14 - Negative ToF-SIMS spectrum of untreated PEEK specimen.

Figure 15 - Negative ToF-SIMS spectrum of PEEK treated at $9.99 \times 10^6 \text{ W mm}^{-2}$

Figure 16 - ToF-SIMS spectra of PEEK specimen, taken from the bulk, between a) 146 and 148 mass units, b) 220 and 223 mass units, c) 280 and 282 mass units