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RESEARCH ARTICLE

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Effect of nitrogen plasma treatment on the crystallinity and self-bonding of polyetheretherketone (PEEK) for biomedical applications

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Polyetheretherketone (PEEK) is a thermoplastic material with outstanding properties and high potential for biomedical applications, including hermetic encapsulation of active implantable devices. Different biomedical grade PEEK films with initial degree of crystallinity ranging from 8% to 32% (with or without mineral filling) were inspected. PEEK surfaces were treated with nitrogen RF plasma and the effects on materials crystallinity and self-bonding were evaluated. In particular, the relationship between auto-adhesive properties and crystalline content of PEEK before and after plasma treatment was examined.

PEEK samples showed different bonding strength depending on their degree of crystallinity, with higher self-bonding performance of mineral-filled semi-crystalline films. XRD did not show any modification of the PEEK microstructure as a result of plasma treatment, excluding a significant influence of crystallinity on the self-bonding mechanisms. Nevertheless, plasma surface treatment successfully improved the self-bonding strength of all the PEEK films tested, with larger increase in the case of semi-crystalline unfilled materials. This could be interpreted to the increase in chain mobility that led to interfacial interpenetration of the amorphous phase.

KEYWORDS

polyetheretherketone (PEEK), plasma surface treatment, self-adhesion, crystallinity, thermal analysis

1 | INTRODUCTION

Polyetheretherketone (PEEK) is a high-temperature thermoplastic polymer, part of the polyaryletherketones family. It can be produced to have a crystallinity degree up to 47 % ca.[1]

PEEK is an attractive material in many contexts, since it presents several very interesting characteristics, like high mechanical properties, combining strength, stiffness, hardness and toughness, depending on polymer crystallinity.[2] Moreover, PEEK shows thermal stability up to more than 300°C and high resistance to chemicals and radiation, a low degree of water permeability, as well as low gas and moisture penetration.[3]

PEEK-based materials, with or without addition of fillers (e.g. mineral, carbon or glass fibres), have been used as alternative to titanium in medical implants, such as spine cages, bone screws, pins, hip stem components, etc.[4] Due to its exceptional physical-chemical properties, together with good biocompatibility and easy of processing by injection moulding, extrusion or thermoforming, PEEK is also suitable for the encapsulation of active implantable medical devices, such as pacemakers, defibrillators, neurostimulators, cochlear implants, etc..[5]

Polymers represent a good alternative to metallic casings, thanks to their good electrical insulation properties and absence of inflammatory reactions related to the release of metallic ions. Among polymers, PEEK is regarded as polymer of choice for producing housings for electronic devices and sensors, due to its processability into thin precise components and low gouging in respect to softer materials (e.g. HDPE or PTFE), although having a higher coefficient of friction.[6] Additionally, PEEK high mechanical properties are well preserved even after sterilization.[7,8]

In order to create protective shells that can safely encapsulate medical devices with electronic components, hermetic bonding of the implant components and joints are required. A tight sealing has to be created, to avoid debonding or formation of leaks that could severely compromise the device performance and patient's safety. Different welding techniques have been applied to PEEK specimens, including ultrasonic, vibration and laser welding, hot plate welding, and adhesive bonding.[9,10] Since the use of adhesives is highly discouraged in the case of biomedical applications, due to potential toxic effects and poor bonding integrity, heat sealing is preferred, but working parameters have to be carefully selected depending on the specific material to obtain optimal sealing.

Autohesion (or self-bonding) refers to the process that allows two pieces of the same polymer to weld by simply pushing the two pieces in contact. It usually takes place just above the glass transition temperature of the polymer and requires long contact times, except in the case that other parameters (like working pressure) are varied. The process is ruled, in the case of amorphous polymers, by reptation theory, which describes the motion of linear polymeric chains in an entangled matrix,[11,12] and by intermolecular diffusion across the interfaces of two thermoplastic layers in intimate contact.

In the case of PEEK polymers, self-bonding and consolidation can be achieved through hot press under controlled working conditions.[13,14] However, due to the presence of non-polar groups, PEEK is characterized by low surface energy,[15] with unfavourable consequences for auto-adhesion processes.

Chemical and physical surface treatments, such as plasma, corona or chemical etching, are frequently used to increase polymer surface energy and to introduce functional groups on the surface.[16]

In this work, we compared three different commercially available PEEK films, with different initial degree of crystallinity, and attempted at modifying their surface by plasma treatment using nitrogen gas as precursor. We aimed at evaluating the effects of plasma treatment on the self-bonding strength of the PEEK samples, and investigated the relationship between auto-adhesive properties and crystalline content of PEEK before and after plasma treatment.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Three different PEEK films were purchased from Victrex plc, namely Aptiv® 2000, Aptiv® 1000 and Aptiv® 1102. According to the manufacturer's technical sheets, the materials are reported to be amorphous, semi-crystalline and mineral-filled semi-crystalline PEEK films, respectively. Thickness and labels of the different samples tested in the study have been reported in Table 1.

2.2 | Methods

2.2.1 | Plasma treatment

PEEK films were cut into 100 mm x 100 mm square samples and wiped with an ethanol-soaked tissue. After surface cleaning, the samples were introduced into a capacitively coupled RF plasma reactor equipped with a vacuum system with a MKS mass flow rate controller.

Preliminary measurements have been conducted to define the more effective parameters for the plasma treatment. N_2, O_2 and Ar were tested as precursor gases and different plasma treatment times were evaluated. According to these preliminary experiments, plasma treatment with nitrogen gas for 2 min was selected for this study, because it showed the most promising results.

The reactor chamber was first evacuated to 0.12 mTorr, and purged with nitrogen gas. The chamber was then filled with nitrogen at a flow rate of 38.3 cm^3/min to obtain an operating pressure of 5.0 mTorr ca. The films were treated for 2 min with cold nitrogen plasma at room temperature generated by a RF power supply operating at 13.56 MHz and 100 W output power. Then the chamber was vented to atmospheric pressure and samples were extracted and stored for following experimental procedures.

2.2.2 | Temperature-modulated differential scanning calorimetry (TMDSC)

PEEK samples were analyzed with TMDSC in order to study the thermal behavior of films and to measure their degree of crystallinity.

Thermal analysis was performed with a DSC 2920 (TA instruments, USA) instrument. For each test, about 10 mg of polymer film were

TABLE 1 Samples tested in the study and related labels

Sample		Label	
PEEK film	Thickness (μm)	Untreated	N_2 plasma treated
APTIV® 2000	250	A	p-A
APTIV® 1000	500	B	p-B
APTIV® 1102	125	C	p-C

introduced in hermetically-sealed Al DSC pans. Aluminium pans with a difference in weight less than 0.02 mg were used as reference. A heating ramp of 5°C/min with 0.56°C modulation temperature amplitude and 60 s period was used, in order to obtain a heating modulated temperature profile. Baseline calibration was performed regularly with empty pans at 5°C/min, and temperature calibration was performed with an indium standard.

Percent crystallinity of polymeric films was calculated from DSC measurements with the formula:

$$\chi_C(\%) = \frac{H_{f(measured)}}{H_{f(100)}} \times 100 \tag{1}$$

where $H_{f\,(measured)}$ represents the heat of fusion obtained from integration of both the exothermic and the endothermic heat flow in reversing and non-reversing TMDSC signals, and $H_{f\,(100)}$ represents the heat of fusion of 100% crystalline PEEK, which was assumed to be 130 J/g.

2.2.3 | X-ray diffraction (XRD)

PEEK films were analyzed with an APD2000 XRD diffractometer (Italstructures, IT) with Cu Kα radiation (λ = 1.5418 Å) generated using 40 kV and 30 mA power supply. Both conventional Bragg-Brentano (B-B, θ/2θ scan) and glancing angle (GA, Ω 0.3°) configurations have been used to acquire XRD spectra with different penetration ability of the incident beam. XRD patterns were acquired with fixed θ and scan 2θ over an angular 2θ region from 10 deg to 35 deg in steps of 0.02 deg for 10 s.

All experimental XRD curves were fitted using a linear combination of Gaussian and Lorentzian (pseudo-Voigt) functions. Background intensity was subtracted by a linearly interpolated background approach before peak-fitting procedure. Crystalline and amorphous halo components have been successfully separated.

The crystallinity index (χ_c) was estimated from XRD spectra as the ratio of crystalline area to total (crystalline and amorphous) area by the equation:

$$\chi_C(\%) = \frac{A_c}{A_c + A_a} \times 100 \tag{2}$$

where A_c is the area under the crystalline peaks and A_a is the area under the amorphous halo.

The average crystallite size for each sample was derived from the X-ray line broadening using the Sherrer equation after accounting for the instrumental peak broadening.

2.2.4 | Self bonding

Both untreated and plasma-treated PEEK films were cut into rectangular stripes (40 mm × 10 mm). Two specimens from the same

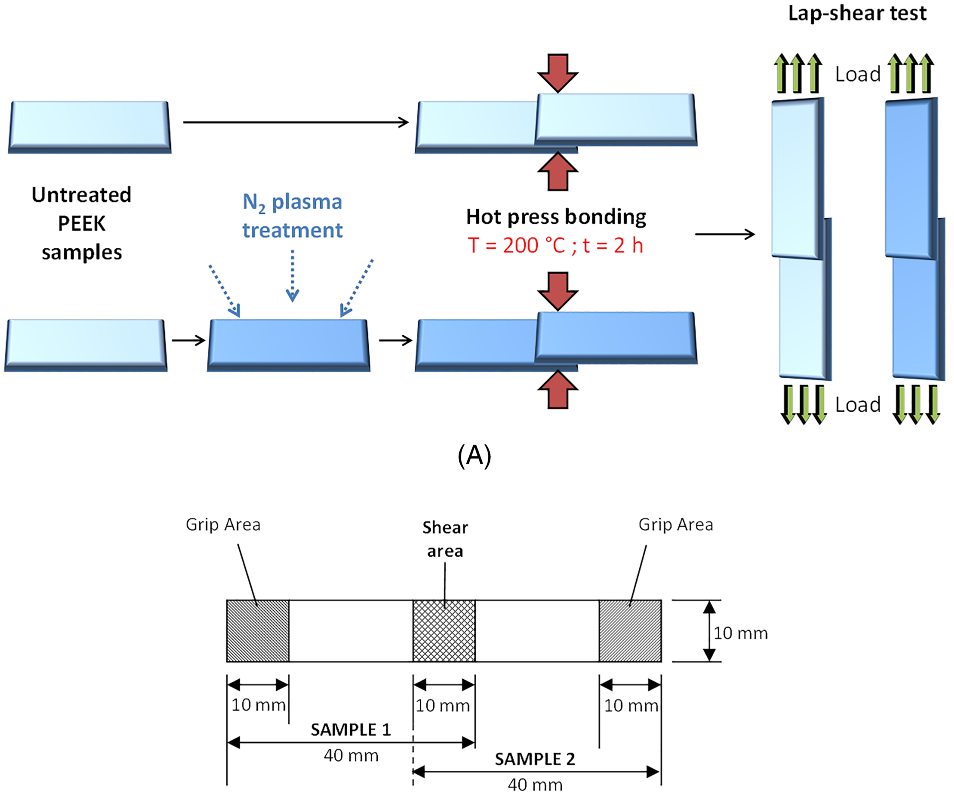


FIGURE 1 A, Schematic representation of samples treating and testing for adhesive strength. B, Configuration of the specimens used for the lap-shear tests – Top view. [Colour figure can be viewed at wileyonlinelibrary.com]

polymer film were partially overlapped (10 mm x 10 mm contact area) and placed in a temperature-controlled hydraulic compression/lamination press (MTP-14, Tetrahedron Associates Inc. USA). The final bonding configuration is reported in Figure 1b. Polymer specimens were maintained in the press at 200°C and 3 MPa operating pressure for 2 h or 7.5 h. [14,17,18]

It is worth to notice that no adhesive was added, in order to test self-adhesion ability of PEEK samples.

2.2.5 | Single lap-shear test

Following bonding process in the hot press, the specimens were examined with the single lap-shear test, which is one of the most used tests for determining adhesive strength of materials and joints.

The test specimens (100 mm^2 shear area) were fixed to the grips of a Instron 5567 testing machine (1 KN load cell) and pulled at a cross head speed of 2 mm/min until failure. Maximum values of failure load and type of failure have been recorded. Samples bonding strength was calculated normalizing the maximum load at failure by the specimen bonding area.

3 | RESULTS AND DISCUSSION

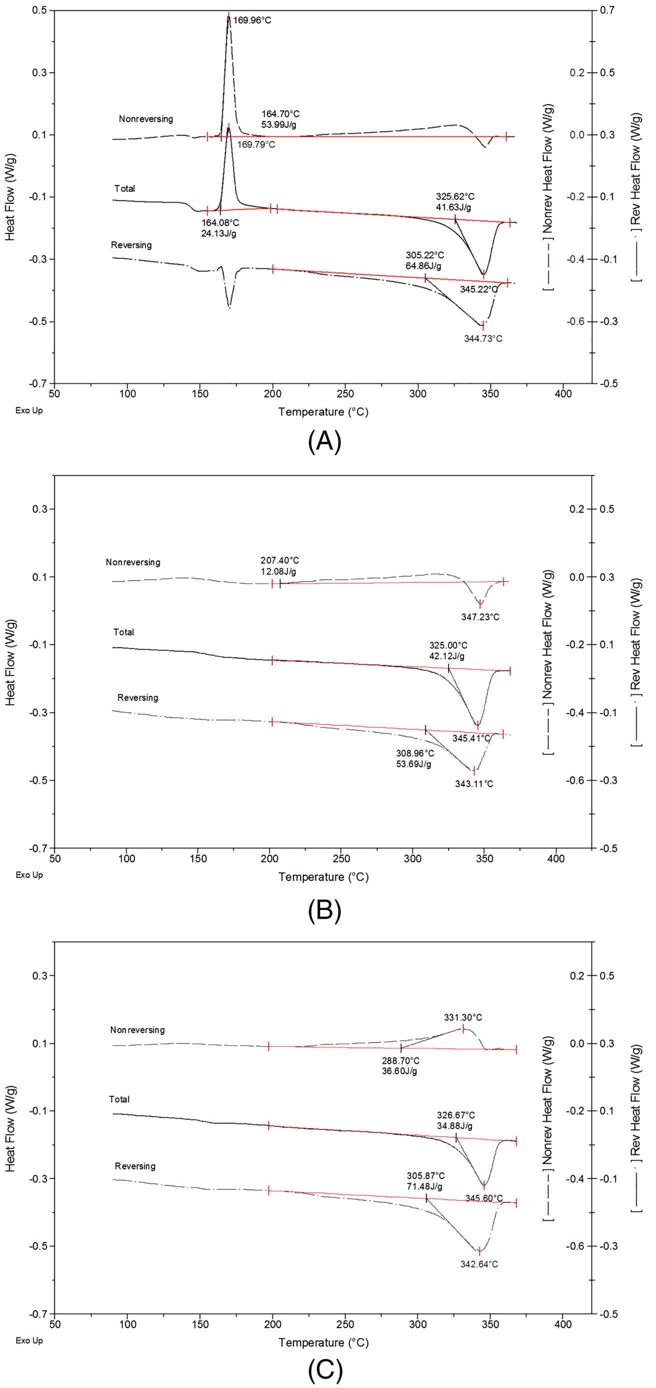
Highly crystalline polymers present restricted mobility of molecular chains, and consequently reduced adhesion strength. In this work we aimed to study the relationships between crystallinity and self-adhesion of PEEK polymer films, and the effects of plasma treatment on these phenomena.

The crystallinity index is an important parameter for polymers, as it affects many physical properties, including polymer density, melting point, hardness, elastic modulus, tensile strength, stiffness and permeability. Polymer crystallinity is also supposed to influence autohesion phenomena,[14] although self-bonding highly depends on processing parameters, including bonding method, working temperature, pressure and time.

3.1 | Thermal properties and crystallinity of PEEK samples

Figure 2 shows TMDSC curves of PEEK samples after the first scan, including total heat flux curves, reversing and non-reversing components. The reversing heat flow represents reversible transition processes, while non-reversing heat flow is particularly useful for determining irreversible processes such as annealing or crystallization during melting.

Temperature modulation guarantees increased resolution and sensitivity respect to conventional DSC, thus TMDSC is very accurate in the measurement of some thermal phenomena which may otherwise overlap, such as glass transitions and enthalpic relaxation.[19]



(A)

(B)

(C)

FIGURE 2 A, TMDSC curves. Reversing, non-reversing and total heat flux of PEEK sample A. B, TMDSC curves. Reversing, non-reversing and total heat flux of PEEK sample B. C, TMDSC curves. Reversing, non-reversing and total heat flux of PEEK sample C. [Colour figure can be viewed at wileyonlinelibrary.com]

Data about basic thermal transitions undergone by the PEEK films are summarized in Table 2. All the samples showed similar melting temperature around 345°C. Of special importance are the thermal events occurring in the range of temperature between 140°C and 220°C, as this is the range in which self-bonding experiments are carried out, with a hot press working temperature of 200°C. In this range of temperature we can notice, for all the samples, the typical thermal curve shoulder related to the glass transition event. Sample A registered a glass transition temperature of 144.1°C, quite lower compared with samples B and C (153°C ca). The total and non-reversing heat

TABLE 2 TMDSC data of the different samples tested

Sample	T_g (°C)	T_c (°C)	T_m (°C)	X (%)[a]
A	144.1	170.0	345.2	38.4
B	153.8	N/A	345.4	32.0
C	152.5	N/A	345.6	26.8

[a] Percent crystallinity was calculated considering a heat of fusion of 130 J/g for 100% crystalline PEEK.

flow curves related to sample A clearly showed a sharp exothermic peak centred at 169.9°C, in correspondence of an endothermic peak in the reversing signal (Figure 2a). This behavior might be attributed to molecular re-arrangement and enthalpy relaxation and indicates that the polymer A undergoes some degree of cold crystallization. The presence of non-reversible transitions was not observed in TMDSC curves of samples B and C, thus excluding cold crystallization processes to take place for these samples.

An endothermic peak corresponding to polymer melting appeared at about 345°C in the total and reversing heat components of sample A, in correspondence of a shoulder with a smaller endothermic peak in the non-reversing component of the heat flow. A similar behavior in the temperature region above 250°C of DSC scans was shown also for samples B and C (Figs 2b and c), with an endothermic melting peak at 345°C in the total and reversing heat flow components and a slightly higher endothermic peak in the same region in the non-reversing heat flow component of sample C.

The initial degree of crystallinity of untreated materials was calculated subtracting the contribution of the non-reversing exothermal peak (enthalpy of the cold crystallization phase transition) from the endothermic reversing fusion peak, as related to the heat of fusion of 100% crystalline PEEK polymer (130 J g^{-1}) (Equation 1).

Percent crystallinity of sample A (8.4 %) was considerably lower than the crystallinity of samples B (32.0 %) and C (26.8 %). There are some indications that the presence of crystalline structures in sample A, mainly amorphous, may be due to a trans-crystalline region that might have been formed during processing.

According to TMDSC measurements, the initial crystallinity of sample A increased extensively (to more than 32 %) when the sample was heated above T_g. For bonding applications at mid-high temperature conditions it has to be considered that the cold crystallization process of PEEK film A is not reversible unless the polymer is re-melted.

Crystal structures and crystallinity index of untreated and plasma treated PEEK samples were investigated by X-ray diffraction. The XRD spectra acquired with B-B geometry of A and B PEEK samples are reported in Figure 3. No diffraction peaks were observed in the case of sample A, which exhibited a broad halo, typical of amorphous structures, centred around 18.5 deg 2θ position. On the other hand, samples B presented the distinctive profile of semi-crystalline polymers, with well-defined peaks due to scattering from crystalline regions superimposed to a broad halo due to the amorphous phase. Diffraction peaks were assigned to (110), (111), (200) and (211) reflections of PEEK. An additional very sharp structure at about 29.1 deg was observed in all the patterns acquired using the conventional B-B geometry, probably originating from the inner layer of PEEK. XRD profiles of sample C exhibited high noise-to-signal ratio.

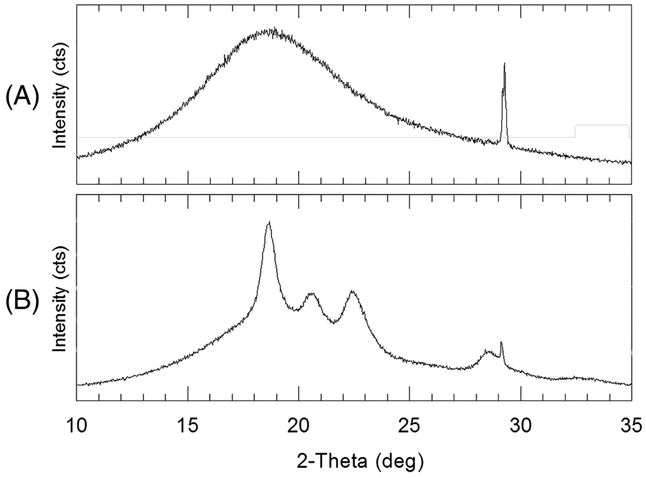


FIGURE 3 X-ray diffraction patterns of PEEK samples A (a) and B (b). Spectra acquired with conventional Bragg-Brentano configuration.

The crystallinity index (χ_c) calculated from XRD measurements confirmed the results achieved with TMDSC, with χ_c values for samples B and C around 36 % and 27 %, respectively. Sample A was almost completely amorphous at the surface. Since XRD analysis is more surface sensitive respect to TMDSC, a slightly higher value of initial crystallinity (8 % ca) registered by TMDSC suggested a higher presence of crystalline domains at the bulk level in the case of sample A.

No significant difference could be detected in the B-B spectra of N_2 plasma treated samples, respect to their corresponding untreated counterparts. In the B-B configuration, X-ray radiation has a large penetration into matter and B-B XRD spectra include information coming from a 5-10 μm thick layer of the specimen. Due to scarce surface sensitivity of the B-B geometry, XRD measurements were repeated using glancing angle configuration (Ω 0.3 deg) to maximize the signal intensity from the surface layers (Figure 4).

Although having higher surface sensitivity, measurements acquired with the glancing angle configuration showed the same structural composition of the samples as conventional B-B measurements, with four main reflections at about 18.7 deg, 20.7 deg, 22.6 deg and 28.7 deg corresponding to the (110), (111), (200) and (211) crystalline planes of orthorhombic PEEK. Small incidence angle arrangements showed a lower average crystallinity (about 4 points %) than that obtained with deepest X-ray penetration (B-B), suggesting a higher contribution of bulk to the material crystallinity.

Both B-B and GA spectra did not show noticeable changes in the crystallographic structure of the untreated and plasma treated semi-crystalline PEEK for all the samples tested. The measured position, FWHM and interplanar spacing values presented no substantial differences for samples analyzed before and after plasma treatment. Only a slight decrease in crystallinity from 27.6 % to 25.9 % was registered in the case of sample B.

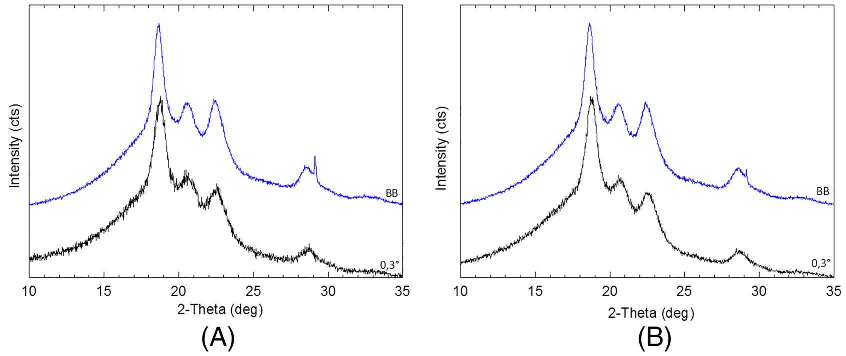


FIGURE 4 XRD patterns of sample B acquired by 0.3 deg GA (black line) and B-B configuration (blue line). A, Untreated and B, N_2 plasma treated films. Spectra were normalized and y-axes shifted for clarity. [Colour figure can be viewed at wileyonlinelibrary.com]

3.2 | Bonding strength of treated and untreated samples

Autohesive potential following hot press bonding of PEEK films was tested through single lap-shear test, as one of the most used standardized analysis to evaluate the performance of adhesives and bonding.

As reported in Figure 5, untreated samples A and B presented a similar bonding strength of about 0.36 MPa, while the untreated mineral-filled sample C presented a significantly higher bonding strength. In the single lap-shear test it was noticed that the specimens from polymers A and B failed by debonding in the overlapping shear area. On the contrary, mineral-filled samples failed at the edge of the shear area while the bonded area stayed intact. Thus samples C failed cohesively, while samples A and B failed adhesively.

Nitrogen plasma treatment significantly improved the bonding strength of all the PEEK films. Upon N_2 treatment the bonding strength of sample A was almost doubled, while autohesive properties raised up to 287 % and 250 % for samples B and C, respectively.

The increase of the hot pressing time from 4 h to 7.5 h at 200°C induced a further improvement of the bonding strength for all the samples. In particular, the bonding strength of the samples A and B showed a significant increase and reached, after 7.5 h, the bonding strength of the mineral-filled sample C around 1.4 MPa ca.

The mineral-filled sample (C) presented the highest bonding strength among untreated samples, despite having lower thickness. The filler used seems to inhibit nucleation in 125 μm thick PEEK films, as shown by a degree of crystallinity 6 % lower respect to the unfilled semi-crystalline material (B). The presence of mineral particles may contribute to limit the growth of crystalline structure, hence allowing for greater mobility of the amorphous portion of the chains and higher interpenetration at the interface with consequent better adhesion.

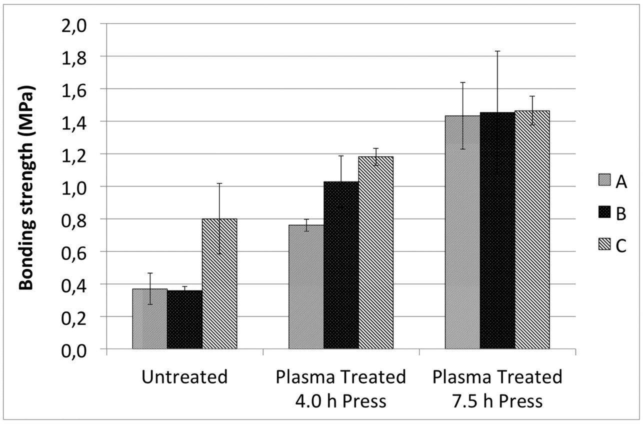


FIGURE 5 Bonding strength results of lap-shear test for untreated and N_2 plasma treated samples.

In the case of amorphous PEEK (sample A), significant changes take place when the polymer is heated above its glass temperature (144°C), as enhanced by the appearance of typical cold crystallization peak in the TMDSC curves around 170°C. The use of hydraulic press at 200°C may therefore allow a substantial surface re-organization and formation of crystalline regions in the amorphous sample. Higher bonding-strength was expected for amorphous PEEK samples, as related to higher chain mobility. However, cold crystallization phenomena seem to have a negative effect on self-bonding of the amorphous sample A, possibly decreasing the mobility and interpenetration of polymeric chains.

According to the results of the present study, welding at 200°C can be ideal for self-adhesion of semi-crystalline PEEK films, while a press working temperature in the interval between T_g and T_c (145-170°C) should be tested in the case of PEEK amorphous samples to check for optimal bonding process parameters. Some evidences, in fact, suggest that a lower degree of cold crystallization could enhance self-adhesion of highly amorphous polymers.

As reported by many authors, plasma treatment is an effective method to induce activation of polymer surfaces and is often used as preparatory step for surface coating or functionalization.[20,21] The interaction of plasma with polymeric surfaces generally induce different surface modifications, including cleaning from contaminants, etching, exposure of functional groups and implantation reactions, radical generation, cross-linking and deposition.[22] The magnitude of these effects depends both on the polymer itself and on the characteristics of the plasma, including type of reactor, gas used to generate the plasma, and process parameters (e.g. gas flux, exposure time, etc.). We think that some of these phenomena have a key role in the adhesion mechanisms and contribute to enhance the bonding strength of PEEK specimens. Several studies reported enhanced adhesion properties of polymers treated with different plasma sources. For example, atmospheric plasma was reported to enhance the adhesion characteristics of low-density polyethylene (LDPE) and poly (ethylene terephthalate) (PET) by a factor of two to ten.[23] The adhesion performance of polyethylene PE-PE joints were also improved by surface activation through atmospheric plasma treatment,[24] and this result was ascribed to combined abrasion and functionalization effects of plasma.

According to our measurements, nitrogen plasma significantly increased the strength of self-bonding for all the PEEK samples, with a stronger effect on semi-crystalline pure and mineral-filled samples (p-B and p-C) respect to amorphous samples (p-A). However, the observations derived from XRD analyzes indicate that the plasma treatment had little, or not measurable, effect on the crystalline structure of semi-crystalline PEEK samples. The effects of nitrogen plasma seem not to be related to a change in the polymer crystalline structure. If any changes in the PEEK microstructure have occurred, they should have taken place in the very top surface layers, since they were not detectable with XRD both in B-B and GA configurations.

Although several studies reported that plasma destroys the crystalline structure of polymers, thus facilitating the mobility of amorphous chain portions and self-bonding, this seems not to be the case of PEEK treated using N_2 plasma at the experimental conditions used in this experimental session. Since PEEK crystalline structure is maintained following nitrogen plasma treatment, the increase of auto-adhesive properties for these samples should be attributed to other physical and chemical modifications induced by plasma. In particular, plasma may activate PEEK surfaces, increasing their surface energy and allowing greater interfacial interpenetration of the polymeric molecules during welding at an operating temperature well above the T_g of the materials tested. Differential action of plasma on amorphous and crystalline domains may produce effects on surface topology, inducing higher mechanical interlocking on semi-crystalline PEEK. Moreover, surface grafting of different functional groups and formation of radicals that can crosslink during the welding process may contribute to the self-adhesion mechanism of PEEK films.

4 | CONCLUSION

In this study, the properties of three different biomedical grade PEEK polymers were investigated. Following TMDSC and XRD studies, the PEEK samples were characterized as: a predominantly amorphous film with an initial residual crystallinity around 8 %, a semi-crystalline polymer (χ_c = 32 %), and a mineral-filled PEEK with a degree of crystallinity of about 27 %.

Self-bonding ability of these materials was assessed, as a crucial characteristic for applications where hermetic sealing is required. PEEK samples presented different bonding strength depending on their degree of crystallinity. In general, higher crystallinity content corresponded to lower values of maximum load at failure, as related to low mobility and scarce interfacial interpenetration ability of polymer chains. However, the samples with the lowest initial crystallinity (8 %) presented poorer bonding strength than expected, as probably due to the occurrence of cold crystallization phenomena during hot welding. The presence of mineral fillers facilitated the formation of tight junctions both in untreated and plasma treated PEEK samples, allowing mineral-filled samples to reach failure through cohesive mechanism at significantly higher values of maximum load.

No significant changes in the materials microstructure and crystallinity have been observed by XRD measurements as a result of the plasma treatment, although we used XRD measurements at different angles. More surface-sensitive techniques should be used to investigate the crystalline behavior ate the interface.

However, nitrogen RF plasma was highly effective at increasing self-bonding strength of all the PEEK samples, as a result of chemical and physical effects, including mechanical interlocking, interfacial interpenetration of the amorphous phase, functionalization and radicals cross-linking.

In conclusion, PEEK self-adhesive properties can be significantly improved through nitrogen plasma treatment, when a careful optimization of treatment and welding parameters is carried out taking in account the initial degree of crystallinity and thermal behavior of the polymer.

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