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Effects of environmental ageing on the static and cyclic bending properties of braided carbon fibre/PEEK bone plates

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ABSTRACT

The use of titanium and steel bone plates to fix fractured limbs can create problems due to stress shielding, bone resorption and subsequent refracture. Here, braided carbon fibre reinforced poly-ether-ether-ketone (CF/PEEK) was evaluated as a possible implant material that could reduce these problems. CF/PEEK bone plates were aged in a simulated body environment for up to 12 weeks and then mechanically tested in 3 and 4-point bending tests. Sample mass increased by around 0.3 wt.%, yet bending stiffness and strength remained unchanged. Scanning Electron Microscopy (SEM) showed no changes in failure modes with age. Braided CF/PEEK shows an excellent resistance to fatigue failure even after prolonged ageing, easily surpassing the fatigue life of commonly used stainless steel alloys such as 316L. In addition, CF/PEEK had half the stiffness of steel for the same static strength, which would reduce stress shielding. Together, the results suggest that CF/PEEK is a highly suitable material for bone plates and should be further investigated for this application.

1. Introduction

Internal fixation of bone fractures using metallic bone plates is common practice, though refractures upon plate removal can occur. This has been attributed to stress shielding [1,2], whereby insufficient physiological load on the bone, due to the high stiffness of the metallic plate, leads to bone resorption. In order to prevent this bone resorption, the use of a material with an elastic modulus similar to that of bone has been proposed [1]. Animal studies have shown that better healing is achieved when low modulus materials such as polymer-matrix composites are used [2]. However, early attempts using carbon fibre reinforced epoxy were unsuccessful because unreacted monomers leached out of the matrix causing a toxic response in the animal subjects [1].

To avoid such toxic responses, attention has focused on thermoplastic composites such as carbon fibre reinforced poly-ether-ether-ketone (CF/PEEK), in the form of braided fabrics or unidirectional sheets. Braided fabrics have several mechanical advantages over unidirectional sheets, such as a lower risk of shear fractures along the fibres and the option to incorporate screw holes without breaking the yarn continuity, thus increasing the overall strength of the composite [3]. This, along with the proven excellent mechanical properties of CF/PEEK [4–6] allows the manufacturing of low-stiffness, high-strength bone plates with a minimal cross-section, which may also facilitate implantation into the limited space between bone and muscle [4].

Chemical and mechanical properties of both PEEK and unidirectional CF/PEEK have been widely investigated [5–13] and both materials had excellent biocompatibility [5,14,15]. Recently, PEEK has found commercial application for spinal implants [9]. However, neither the static nor the dynamic mechanical properties and failure mechanisms of braided CF/PEEK are well-understood, making it uncertain whether or not this material has the necessary strength for use in the fixation of fractures. Also, little is known about the short and long term effects of water and saline solutions (like body fluids) on the fatiguing behaviour of CF/PEEK composites, a crucial feature for bone fixation plates [16–18]. Knowing and understanding these properties is essential for their use in implants. To address theses issues, this study investigates the flexural properties of CF/PEEK bone plates prior to, and after ageing for several months in a simulated body environment (SBE; defined here as 0.9% NaCl at 40 °C).

2. Methods

Experiments were performed on braided CF/PEEK bone plates designed for implantation in the human shinbone. The plates were manufactured with a simple braiding technique. PEEK and carbon fibres were commingled and braided into a flat fabric with a

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Table 1
Ageing environment, ageing time and subsequent destructive and non-destructive test methods for all specimens

Ageing environment	Number of specimens	Ageing time	Mass monitoring	Stiffness monitoring	Destructive test method
0.9% NaCl – 40 °C	2	12 weeks	Yes	Yes	Static
0.9% NaCl – 40 °C	2	14 weeks	Yes	Yes	Fatigue
0.9% NaCl – 40 °C	2	8 weeks	No	No	Static
0.9% NaCl – 40 °C	1	8 weeks	No	No	Fatigue
Water – 40 °C	1	12 weeks	Yes	Yes	Static
Atmosphere – 25 °C	1	14 weeks	Yes	Yes	Static
0.9% NaCl – 90 °C	2	3 days	Yes	No	Static
Atmosphere – 90 °C	2	3 days	Yes	No	Static
No ageing	2	–	No	No	Static
No ageing	3	–	No	No	Fatigue

diamond braiding structure. Six layers of fabric were stacked and hot pressed in a stainless steel mould with attached pins that formed holes without breaking the yarn continuity. A detailed description of the manufacturing process can be found in Fujihara [4]. The specimens were 103 mm long and 15 mm wide, with a thickness ranging from 3.18 to 3.32 mm. The braiding angle was 10°, and the average specimen density was 1.567 ± 0.004 g/cm^3.

Specimens were aged in a variety of different environments (Table 1). Seven specimens were immersed in SBE for 8–14 weeks; one specimen was aged in water at 40 °C for 12 weeks, and one sample was aged in atmosphere at room temperature (around 25 °C) for 14 weeks. Since this ageing time was relatively low for plates that normally stay in the body for 6–12 months, accelerated ageing experiments were also performed. Two specimens were aged at 90 °C for three days in saline solution and another three in atmosphere at 90 °C for three days. A further five specimens did not undergo any ageing and were used as a reference.

Changes in mass and flexural modulus were measured periodically during the ageing time. Stiffness was measured using non-destructive 3-point bending tests. This test followed the procedures of ASTM D790-07 [19], with the exception that the load was not increased until specimen failure, but kept low enough to prevent plastic deformation. In addition, the rollers were curved to match the curvature of the specimens to prevent local indentation. From the load versus deflection curve, an equivalent flexural modulus (EFM) was calculated using the equations for standard flat specimens [19] having the same cross-section area as the bone plates.

After ageing, static and fatigue strength were measured using destructive 4-point bending tests. The number of specimens used for each test method is listed in Table 1. To measure the static strength, destructive 4-point bending tests were carried out in accordance with ISO 9585 [20]/ASTM F382 [21] after the ageing was completed. From the static test data, bending stiffness (BS), yield bending moment (YBM) and maximum bending moment (MBM) were calculated as given in Laurence [22] and Fujihara [4]. Fatigue tests were performed with the same 4-point bending setup, but with a sinusoidal loading mode ($R = 0.1$ $f = 1$ Hz). Cycles to failure at 75–100% of MBM were measured. Failure mechanisms were analyzed using Scanning Electron Microscopy (SEM) of the fracture surfaces after destructive testing.

3. Results

Upon immersion in either SBE or water at 40 °C, all specimens showed an increase in mass (Fig. 1A). After 12 weeks of ageing, specimens in SBE showed a mass gain of 0.23 ± 0.05 (1σ, $n = 5$) wt.%, and the specimen aged in water showed a mass gain of 0.32 wt.%. A reference specimen kept in atmosphere had a slight mass gain of 0.04 wt.%. Specimens aged in 90 °C saline had a mass gain of 0.33 ± 0.08 wt.% (1σ, $n = 2$) in just three days, nearly 50% higher than any of the other specimens. Ageing at 90 °C in atmosphere caused a mass loss of 0.06 ± 0.02 wt.% (1σ, $n = 2$).

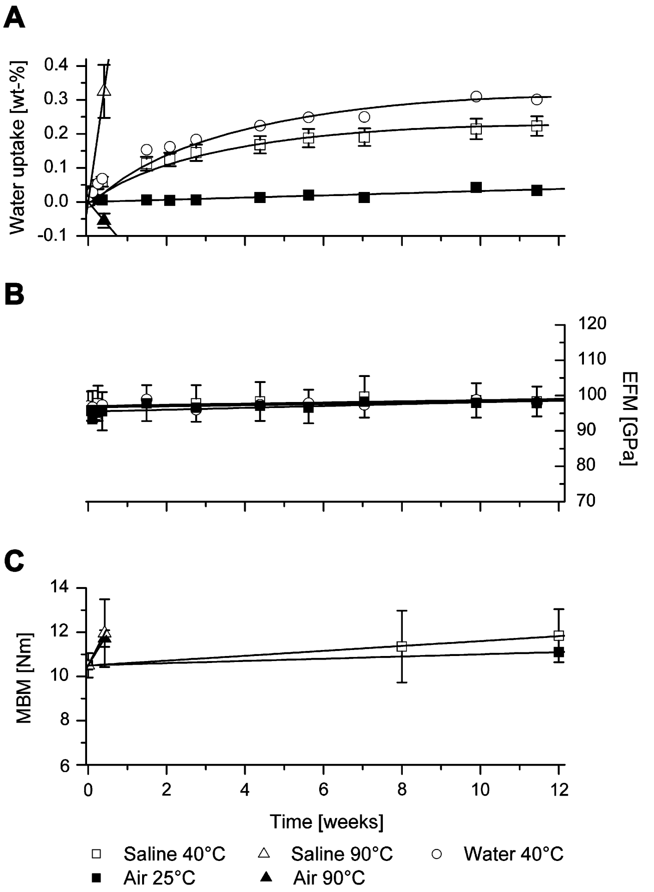

Fig. 1. Changes in (A) mass, (B) equivalent flexural modulus and (C) maximum bending moment over 12 weeks for specimens aged in different environments. The mass (A) of specimens changed depending on the ageing environment. Both EFM (B) and MBM (C) remain unchanged within error for all ageing conditions. Error bars represent ±1 standard deviation where more than one specimen was used.

Despite the changes in mass, both EFM and the strength of all specimens were unaffected by ageing, regardless of inversion environment (saline, air or atmosphere) (Fig. 1B). Results from destructive 4-point bending tests showed that the MBM increased by 1.3 Nm during 14 weeks (Fig. 1C), which is within error of the non-aged samples. Failure always occurred next to a screw hole, where the cross-section of the plate is reduced.

All specimens (aged and non-aged) exhibited a high resistance to fatigue failure (Fig. 2), as indicated by the gentle slope of the load versus cycles plot. At 75% of the static strength, failure was

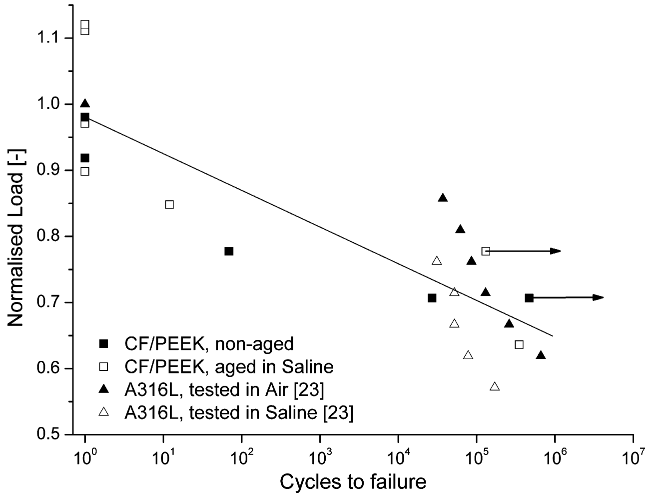

Fig. 2. Changes in normalised load with cycles to failure for CF/PEEK bone plates and stainless steel specimens [23]. A linear fit with combined results from all CF/PEEK specimens (aged and non-aged) was added to aid visualisation. Arrows indicate where specimen failure was not reached. These results show the excellent resistance to cyclic loads of braided CF/PEEK. All data points were normalised by dividing the fatigue loads by the ultimate strength of the respective material (A316L: 1050 MPa, CF/PEEK bone plates: 11.3 Nm).

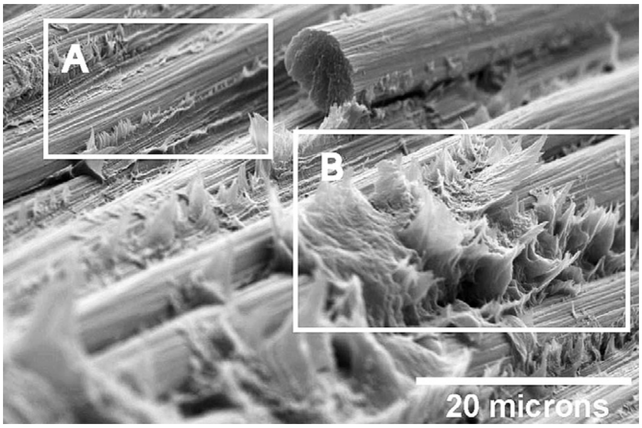

Fig. 4. High magnification of the fracture surface of a specimen after a destructive 4-point bending test showing the two failure mechanisms in tension: failure in the fibre–matrix interface (area A) and failure within the matrix (area B). If the interface fails (area A), the fibres separate from the matrix, with only small pieces of PEEK still attached. Failure in the matrix (area B) is characterized by high plastic deformation of the matrix. Often, as shown here, both failure mechanisms occur simultaneously.

not reached even after more than 300,000 load cycles, further supporting the notion of CF/PEEK's good fatigue properties. For comparison, values from tensile fatigue tests for the commonly used stainless steel A316L [23] were added to Fig. 2.

SEM analysis of the fracture surfaces of specimens both from static and fatigue experiments revealed two failure modes: tensile and compressive failure, as is usual for a bending test. Tensile failure, the primary failure mode (bottom two thirds of Fig. 3A), is characterized by a very rough fracture surface, where individual fibre bundles (former yarns in the braid) seem to have debonded and failed individually. On a larger magnification (Fig. 3B), concentric crack growth on the fibre surfaces can be made out. Within the tensile area, two different failure mechanisms occurred, failure in the matrix–fibre interface (Fig. 4A) and failure within the matrix (Fig. 4B). Interfacial failure is characterized by individual carbon fibres that have been completely stripped off the matrix (Fig. 4A), whereas matrix failure typically leaves the fibres with small bits of matrix still attached (Fig. 4B). Often, as shown in Fig. 4, both failure mechanisms occur simultaneously.

Compression, the second failure mode, accounted for around 10–20% of the fracture surface and is characterized by a smooth fracture surface that passes through fibres and matrix alike (Fig. 3A). In contrast to the tensile failure, the fibres show an angular fracture surface (Fig. 3C). No evidence of fibre buckling or kinking was found. In addition, ageing history appears to have no effect on either the failure modes or mechanisms.

No significant differences between test methods were found either; the fracture surfaces of specimens from static and fatigue tests appeared fairly similar. However, a somewhat higher degree of matrix failure was observed in fatigue specimens. No clear crack initiation site could be found.

4. Discussion

4.1. Water absorption

Complete saturation was not reached for any specimen after 12 weeks, suggesting that moisture absorption in CF/PEEK occurs very slowly at 40 °C. Raising the temperature to 90 °C, however, greatly

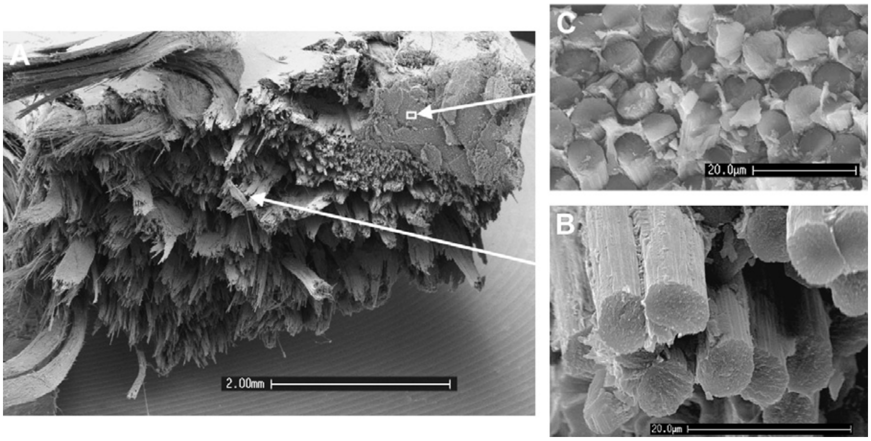

Fig. 3. (A) Frontal view of half the fracture surface of a specimen after a destructive 4-point bending test. Upon implantation, the top surface would be in contact with the bone (compressive side) and the bottom surface face outwards (tensile side). The left-hand side of the image shows fibre bundles curved around a screw hole. Two different failure modes have occurred: compression and tension. (B) Close up of tensile failure on the fracture surface. (C) Close up of compressive failure on the fracture surface.

increased the absorption rate. It is not known whether the measured value of 0.33 wt.% represents the saturation level or not.

The specimen kept in deionised water had a slightly higher increase in mass compared to the seven specimens aged in saline solution. This may be due to the slightly lower density of 1.56 g/cm^3 for that specimen, compared to 1.57 ± 0.04 g/cm^3 for the seven specimens aged in SBE. This lower density, most likely indicating a slightly higher porosity, would promote water absorption. These results are similar to findings for PEEK, where saline content was not found to influence the water absorption behaviour [8].

A reference specimen kept in atmosphere at room temperature also exhibited an increase in mass; though the increase was an order of a magnitude lower (0.04 wt.%) than that of specimens aged in SBE. The mass increase of the reference specimen is only half of that reported for a unidirectional CF/PEEK specimen kept at 65% relative humidity for 6 weeks by Dickson [24]. This difference is probably due to storage at lower relative humidity in this study (around 50%). Storage at 90 °C in atmosphere led to a net loss of moisture, suggesting that the specimens had already absorbed some humidity during fabrication, transport and/or preparation.

The measured moisture absorption values of CF/PEEK in this study (average of 0.35 wt.%) are in the same range as literature values (0.24–0.45 wt.%) [10,24]. The reported saturation level for pure PEEK is 0.5 wt.% [8,25]. Using this pure PEEK percentage and assuming a fibre content of 55 wt.% as for our samples, the calculated maximum water uptake is 0.23 wt.%, much lower than the measured values presented here. Assuming that the carbon fibres do not absorb any water, it is likely that a different absorption mechanism occurs in the composite material. The increased water absorption could be caused by residual stresses in the matrix. Stresses due to different rates of thermal expansion between PEEK and carbon fibres were shown to be as high as 30 MPa [26]. In addition, internal stresses of a similar magnitude can be caused by the anisotropy in thermal expansion for the different layers in a laminate and non-isothermal solidification [26]. These values are relatively high compared to the tensile strength of PEEK, which is only 100 MPa [25]. Therefore, they can lead to substantial deformation of the polymer chains and create a higher volume, allowing water absorption.

4.2. Mechanical properties and fracture surface analysis

Both bending stiffness and strength of CF/PEEK remained largely unchanged after ageing in different environments, despite water absorption by the matrix (Fig. 1B and C). These results are consistent with previous studies that found little or no influence of water content on the mechanical properties of PEEK [27] and CF/PEEK [10,12,24]. The relatively large spread in specimen strength (indicated by the error bars in Fig. 1C) was probably due to the variability in specimen thickness. When measuring the thickness of all specimens included in this study, the standard deviation was around 5%. This variability is probably too high for an implant material; however, further refinement of the manufacturing process should result in more consistent specimen thickness, and thus reduce variability in specimen strength.

The similar failure mechanisms observed for different ageing histories are consistent with similar strength values obtained from mechanical testing (Fig. 1B and C). The water content does not weaken either the matrix or the fibre–matrix interface to an extent that could lead to a measurable strength loss, and this suggests that CF/PEEK bone plates will retain their good mechanical properties upon implantation.

The fatiguing behaviour of fibre reinforced composites is dominated by the matrix and the matrix/fibre interface properties, since carbon fibres are more or less insensitive to fatigue [28]. In this study, only a very small proportion of interfacial failure was observed, and the PEEK matrix has both high ductility and fracture toughness. Thus, CF/PEEK bone plates have a very high fatigue strength, (Fig. 2), despite debonding of individual yarns, which has been found to promote failure [13]. The excellent fatigue properties are retained upon immersion in saline solution. A trend towards slightly increasing fatigue strength with liquid content, as reported by Dickson [24], was not observed here. However, a much smaller number of samples were analyzed in this study, and to verify the nature of changes in fatigue strength with liquid a much larger number of specimens would be necessary. Compared to the widely used stainless steel A316 tested in air, the fatigue behaviour of braided CF/PEEK is similar (Fig. 2). However, stainless steel is susceptible to corrosion in a saline environment, which leads to accelerated crack growth [17,23] and consequently much lower cycles to failure (open triangles in Fig. 2). The combination of corrosion and fatigue has caused failure of steel implants [16–18,29–31]. In summary, the preliminary results presented here indicate that braided CF/PEEK bone plates perform very well under cyclic loading conditions that are similar to physiological loads [32] and in a simulated body environment.

4.3. Suitability for implantation

The high static and fatigue strength of CF/PEEK bone plates after ageing bodes well for its application as an implant material. Furthermore, bone plates made from braided CF/PEEK reached similar yield bending moments to steel plates while having a much lower bending stiffness (Fig. 5). For any given yield bending moment, the bending stiffness of CF/PEEK plates is around 50% lower than that of steel. Previous studies suggested that it would be preferable to manufacture bone plates from materials that have around half the stiffness of stainless steel [33]; results presented here would seem to suggest that CF/PEEK fits this criteria. The lower bending stiffness of CF/PEEK would lead to less shielding of the physiological load from the treated bone, thus minimizing bone resorption. Therefore, refractures upon plate removal would be less likely. A further benefit of the CF/PEEK plates evaluated here is that they have a lower thickness than standard AO steel plates (3.2 mm as opposed to 3.8 mm). This should make it easier to implant them into the limited space between muscle and fragmented bone [4]. The combination of lower stiffness and smaller dimensions makes CF/PEEK bone plates much better suited to implantation than steel plates.

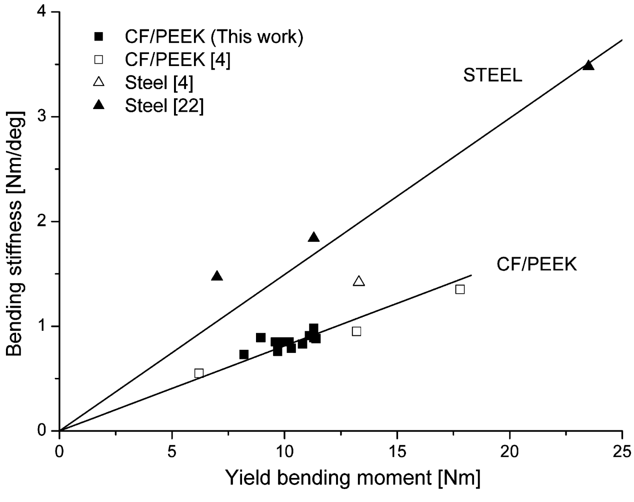

Fig. 5. Comparison of the relationship between yield bending moment and bending stiffness for steel [4,22] and CF/PEEK bone plates [4]. While both materials reach a similar yield bending moment, the stiffness of CF/PEEK plates is only half that of steel plates for the equivalent yield bending moment.

5. Conclusions

1. Mechanical properties of braided CF/PEEK are not affected by immersion in water or saline solution at physiological temperatures over 12 weeks. Both bending stiffness and strength remain unaffected by absorption of saline solution, and the failure modes for the CF/PEEK bone plates are the same for all ageing conditions. This indicates that braided CF/PEEK has an excellent resistance to body fluids, which makes it well suited to implantation.
2. Preliminary fatigue experiments indicate that CF/PEEK bone plates are likely to perform well under physiological loads and when subject to a saline environment.
3. For the same static strength, CF/PEEK bone plates have half the stiffness of steel plates. This means that the more flexible CF/PEEK plates can greatly reduce problems associated with stress shielding, while still offering comparable strength to steel plates.
4. All physical, chemical and mechanical properties investigated in this study make braided CF/PEEK an ideal material for osteosynthesis plates, and it should be further investigated for this application.

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