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Bioactive glass–chitosan composite coatings on PEEK: Effects of surface wettability and roughness on the interfacial fracture resistance and in vitro cell response

Wei Hong¹, Fangwei Guo^{1,*}, Jianwei Chen², Xin Wang³, Xiaofeng Zhao¹, and Ping Xiao⁴

1 School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

2 Department of Orthopedics, Renji Hospital, School of Medicine, Shanghai Jiao Tong University, Shanghai 200240, China

3 Konca Solar Energy Co. Ltd., Wuxi 214174, China

4 School of Materials, University of Manchester, Manchester M13 9PL, United Kingdom

*Corresponding author. E-mail: fwguo2014@sjtu.edu.cn; Tel.: +86 21 54747565; fax: +86 21 5474 7565.

ABSTRACT

To improve the osteointegration of polyetheretherketone (PEEK) spinal fusions, the 45S5 bioactive glass® (BG)-chitosan (CH) composite was used to coat the PEEK by a dip-coating method at room temperature. A robust bonding between the BG-CH composite coating and the PEEK was achieved by a combined surface treatment of sand blasting and acid etching. The effects of surface wettability and surface roughness on the adhesion of the BG-CH composite coating were characterized by fracture resistance (G_c), respectively, measured by four-point bending tests. Compared with the surface polar energy (wettability), the surface roughness ($>3\mu\text{m}$) played a more important role for the increase in G_c values by means of crack shielding effect under the mixed mode stress. The maximum adhesion strength (σ) of the coatings on the modified PEEK measured by the tensile pull-off test was about 5.73 MPa. The in vitro biocompatibilities of PEEK, including cell adhesion, cell proliferation, differentiation, and bioactivity in the stimulated body fluid (SBF), were enhanced by the presence of BG-CH composite coatings, which also suggested that this composite coating method could provide an effective solution for the weak PEEK-bone integration.

KEYWORDS: Polyetheretherketone (PEEK); 45S5 bioglass-chitosan composite coating; surface treatment; four-point bending test; osteointegration

1 INTRODUCTION

Polyetheretherketone (PEEK), a non-resorbable and biocompatible polymer, is a promising candidate for replacing conventional metallic biomaterials for spinal fusion cages [1-3]. However, the applications of PEEK suffer from its natural bioinertness, which usually leads to weak bone-implant integration [4, 5]. Bioactive coatings on PEEK have

Abbreviations

Bioactive glass-BG; chitosan-CH; sandblasting-SL; acid etching-AE; a combination of sandblasting and acid etching-SLA.

been extensively used to improve its bone-implant integration [6-8]. Due to the hydrophilic and chemical inert surface of PEEK, still, the bioactive coatings usually have weak adherence to the PEEK substrate [9], even leading to the interface separation from the surrounding bone after surgery implantation. Some researchers have reported relative good adhesion strength of the bioactive coatings on PEEK [10-12], but these coatings are fabricated by high temperatures techniques (over 400 °C), which result in PEEK deformation considering that the glass transformation temperature and melting point of PEEK are 143 °C and 335 °C respectively [1]. Most of the researches about bioactive coatings on PEEK focus on the biological properties, while the interface bonding behavior and adhesion mechanism of the coatings are lack of a systematic understanding. Therefore, the analysis of various influence factors on the interfacial bonding behavior of the bioactive coatings on PEEK is very important, in order to have a physical stability and robust mechanically adherent coating fabricated at ambient temperatures.

As reported, the adhesion property of PEEK can be improved by different surface treatments, which is dependent on its surface wettability or surface roughness [13-21]. By increasing the surface micro-roughness and number of adhesive surface functional groups, a conventional piranha solution etching and sand blasting treatment can significantly increase the bonding of PEEK [13, 15, 16]. By increasing its surface free energy, laser treatment can also increase the lap shear strength of PEEK [18]. Treatments targeting at adhesion improvement have also been conducted by atmospheric pressure plasma, radio-frequency plasma, etc. [14, 22], but most of them modify the surface energy and surface roughness of PEEK both, at the same time. Therefore, a systematic analysis of whether the surface wettability or surface roughness contributes to the establishment of the interface adhesion of bioactive coatings on PEEK is not clear.

Inspired by the composite structure of natural bones, bioactive glass-polymer composites for coating orthopaedic implants have been investigated [23-25]. 45S5 bioactive glass® (BG) is the first artificial bioactive glass that is able to form a chemical bond with bone and soft tissues [26], providing the composite coatings with bioactivity [27, 28]. In vitro and in vivo studies have shown that the bioactive glasses bond with bone more rapidly than other bioceramics [29]. Chitosan (CH), a natural polysaccharide, is an alternative to collagens in the bone tissue engineering, which can be used as a polymer matrix for embedding bioactive particles [30-33], with its good biocompatibility, antitumor activity, and protein adsorption properties [34]. In addition, composites made of these two biomaterials can overcome the brittleness of the bioactive component and eliminate problems associated with high temperature consolidation of the glass coatings [35]. Therefore, the 45S5 BG and CH composite was used to coat PEEK substrate for improving its biocompatibility and bioactivity in this work.

This paper aims to provide a simple and effective method for preparing bioactive coatings on PEEK with complex shapes (e.g. spinal fusions) at room temperature and to

clarify the adhesion mechanism between the BG-CH coatings and PEEK substrates. Dip coating method was employed owing to the simplicity of its application at ambient temperatures. Chemical etching and sand blasting to the PEEK substrate were explored to expose the initiation sites for coating adhesion. The relationship between the bonding behavior, adhesion mechanism and the substrate surface properties including surface roughness and surface wettability was investigated. Both four-point bending test (mixed mode stress) and pull-off test (mode I stress) were used to evaluate the fracture resistance and adhesion strength of the samples for understanding the interfacial bonding behavior. The coating morphology, physico-chemical properties, bone bioactivity and in vitro cell responses, including cell growth and osteoblastic differentiation, were also studied.

2 MATERIALS AND METHODS

2.1 Surface treatments of the PEEK discs

PEEK discs (Optima® Invibio, UK) were ultrasonically cleaned in acetone and deionized water for 20 min and 10 min respectively, then dried with compressed air. The modified PEEK discs were divided into 3 groups according to the different surface treatments as shown in Table 1, and every treatment contained 6 samples. In Group 1, sandblasting was used to increase the surface roughness, which was performed at a pressure of 30 bar with four sizes of alumina grits (124 μm , 250 μm , 590 μm and 1190 μm). In Group 2, acid etching was conducted to vary the surface wettability in a 2.5% w/v solution of KMnO_4 in H_3PO_4 for several durations [36]. A combination of sandblasting and acid etching was used to treat the discs in Group 3. For short, the PEEK samples modified by sand blasting, acid etching and the combination of sand blasting and acid etching were denoted as 'SL', 'AE' and 'SLA', respectively. After the different surface treatments, the modified discs were washed several times with deionized water prior to further analyses and coating preparation.

2.2 Preparation of the BG-CH composite coatings

45S5 bioactive glass® (BG) ($D_{50} = 25 \mu\text{m}$, Aladdin, China) and chitosan (CH) (95% degree of deacetylation, 100-200 mpa.s, Aladdin, China) were used to prepare the BG-CH composite solution. The commercial 45S5 bioactive glass® powders were dense particles, fabricated by melting technique. The CH powder with 95% higher deacetylation was preferred because of its better performance in the cell adhesion and proliferation [37, 38]. First, 2 wt. % CH were dissolved in 1 wt. % aqueous acetic acid and filtered to remove impurities. Then, 2 wt. % BG particles were added to the solution and the mixture was stirred over 2 hours until a relative stable solution was obtained. Before dip coating,

the composite solution was treated by ultrasonication for 200 s. During the coating process, the BG-CH solution was dynamically stable, maintaining by a magnetic stirring. The modified PEEK discs were dip coated in the composite solution, and then left to dry at room temperature. After drying, the coated samples were neutralized with a 0.1 N NaOH solution and washed with distilled water to remove the residual electrolytes.

2.3 Surface characterization

The surface wettability of the modified PEEK was determined by the calculated surface energy from the contact angle results. Contact angle measurements of PEEK were conducted directly after the surface treatments by using the sessile drop technique (Powereach®, Shanghai, China). Testing liquids were deionized water and ethylene glycol with the surface energies known. Measurements were conducted with 3 drops of each liquid. The resulting surface energy and its components (polar and dispersive parts) were calculated from the contact angle value using the geometric-mean and harmonic-mean method described by Wu [39].

Surface roughness S_a (the arithmetical mean deviation of the profile) of PEEK before and after the surface treatments were analyzed using a non-contact 3D-laser profilometry (Zegage™, Zygo, USA) with 10× objective lens. Each sample was measured 6 times with a measuring area of $834 \times 834 \mu\text{m}^2$. Optical images of surface topography of the modified samples were also provided by the 3D-laser profilometry.

X-ray photoelectron spectroscopy (XPS) (ESCALAB250, Thermo, US) was used to identify the functional groups of the PEEK after the surface treatments. The spectra were recorded by using a 45° take-off angle with respect to the surface normal. All obtained spectra were calibrated to the standard binding energy value of the C1s peak at 284.8 eV.

The surface and cross-section morphologies of the BG-CH composite coatings were examined under a scanning electron microscopy (SEM, FEI Quanta 200, Netherlands) with an acceleration voltage of 10 kV. The samples were gold coated before SEM analysis.

2.4 Fracture resistance and tensile adhesion strength measurements

Fracture resistance (G_c) of the BG-GH composite coatings on PEEK were measured by using the four-point bending test (Zwick-Z20, Ulm, Germany). The interface fracture resistance is a quantitative measure of the bonding strength at a mixed loading stress and theoretically a sum of the intrinsic work of adhesion, roughness-related shielding and plastic dissipation of the materials [40]. The sample for the four-point bending test had a sandwich structure composed of one BG-CH coated PEEK disc and one uncoated PEEK disc, and each disc had the same dimension of $60 \times 4 \times 2 \text{ mm}^3$, as shown in Fig. 1. The uncoated PEEK disc was glued to the top of the coating surface with epoxy glue (Adbest®, Shanghai, China). After cured at 100°C for 3h, a notch at the geometric center

of the samples was made by using a precision cutter to approach the interface between the glue layer and the BG-CH composite coating. The G_c value was calculated by equation (1) [41-43]:

$$G_c = \frac{21(1-\nu^2)M^2}{4Eb^2h^3} \quad (1)$$

where E (3.5 GPa) and ν (0.40) are the elastic modulus and Poisson's ratio of the PEEK substrate, respectively; the bending moment is $M = Pl / 2$, with P being the plateau load and l the spacing between the inner and outer loading lines; b is the beam width, h is the PEEK thickness.

The tensile adhesion strength of the samples (20 mm in diameter) was also measured by using the pull-off test (Zwick-Z100, Ulm, Germany) according to ASTM C633 [44], which is a direct bonding strength at mode I stress. The tensile adhesion fixtures were bonded one on the top side of the BG-CH composite coating and the other on the bottom side of the PEEK substrate with high strength epoxy (Adbest®, Shanghai, China), and then cured at 100°C for 3 h. The bonding strength was calculated according to the equation (2): $\sigma = F / S$, where σ is the tensile bond strength, F is the load (N) at failure and S is the adhesive area (mm²).

2.5 In vitro bioactivity and cell response

The in vitro bioactivity of the BG-CH coated on PEEK (8 mm in diameter) was evaluated by soaking them in a simulated body fluid (SBF), which was prepared according to the method of Kokubo et al. [45]. Each sample was immersed in 5 ml SBF at 37 °C for 1, 3, 7 and 14 days, refreshing the SBF every other day. After removed from SBF, they were gently rinsed with distilled water, dried at room temperature and then inspected by SEM and Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, Thermo Sci., USA).

MC3T3-E1 osteoblast cells were used to investigate the in vitro cellular response of the BG-CH composite coated PEEK. MC3T3-E1 cells (Cell Bank, Chinese Academy of Sciences) were cultured in growth medium consisting of α -MEM supplemented with 10% FBS and 1% penicillin and streptomycin in a cell incubator at humidified atmosphere with 5% CO₂ at 37 °C, with fresh medium replaced every 2 days. MC3T3-E1 cells of third-sixth passage were used for the experiments. The uncoated PEEK was used as the control sample. For characterization of cell adhesion, the sterile samples were placed in 24-well plates with MC3T3-E1 cells seeded on them at a density of 1×10^4 cells/well and then incubated for 24 h. After then, the cells were fixed in 2.5% glutaraldehyde, dehydrated gradually and coated with gold for SEM. The cell proliferation was measured by CCK-8 (Cell Counting Kits) assay. The cells were seeded in a 96-well plate at a density of 2×10^3 cells per well and cultured with 100 μ L extracts of the BG-CH coated PEEK in each well for 1, 3 and 5 days respectively, therewith tissue culture plates were used as the negative control. A total of 10 μ L of CCK-8 dilution (Beyotime, China) was added in each well, and the plates were incubated in a cell incubator for 2 h. The

absorbance of the contents of each well was measured at 450 nm using a microplate reader. Osteoblastic cell differentiation of the BG-CH composite coated PEEK was determined by measuring the alkaline phosphatase (ALP) activity. MC3T3-E1 cells were seeded in a 6-well plate at a density of 1×10^4 cells/well. After culturing the cells for 3, 7 and 14 days, those cells on the samples were gathered and re-suspended by treating them with 0.1% Triton X-100 and a cyclical freezing and thawing process. Each aliquot of the cell lysates was normalized to the total protein content and the ALP activity was measured by means of an enzymatic reaction using a p-nitrophenyl phosphate substrate (pNPP, Sigma-Aldrich, USA). The absorbance was measured at 415 nm and the ALP activity levels were calculated from a standard curve which was obtained with bovine serum albumin in the concentration range 0.2 ~ 1.2 mg/ml.

Statistical analysis of in vitro cell response was carried out using one-way analysis of variance (ANOVA) with statistical significance set at $P < 0.05$ (*) and $P < 0.001$ (**).

3 RESULTS

3.1 Morphology of the BG-CH composite coatings

It was noticeable that after sand blasted with alumina particles, the SL PEEK remained weakly bonded with the BG-CH coating and the coatings peeled off by the end of the drying process. However, the BG-CH coating could adhere on the AE PEEK or the SLA PEEK and possessed good adhesion strength, as shown in Fig. 2. In Fig. 2, BG particles homogeneously distributed in the BG-CH composite coatings on the AE PEEK and SLA PEEK. The average thicknesses of the BG-CH coating on the two PEEK substrates were both about 20 μm . Besides, the cross section of the two samples showed similar morphology at a higher magnification with randomly stacking laminates, as shown in Fig. 2(b) and 2(e).

3.2 Surface roughness of the AE PEEK and the SLA PEEK

Since the BG-CH coatings could not adhere on the SL PEEK, a combination of sand blasting and acid etching (SLA) was used to modify the PEEK surface roughness, as compared with the AE PEEK. Fig. 3 shows the surface roughness (S_a) of the raw PEEK, AE-30 min PEEK and SLA PEEK with four sizes of alumina grits (SLA-124 μm , SLA-250 μm , SLA-590 μm and SLA-1190 μm). The AE PEEK after different etching time did not have significant difference in the surface roughness and only the S_a (0.028 μm) of AE-30 min PEEK was exemplified in Fig. 3, because the S_a of them was in the range of 0.014 μm ~ 0.034 μm and in the same order of magnitude with the raw PEEK (0.058 μm). The relative decrease in the surface roughness of AE PEEK was due to the removal of contaminant surface layer during the etching treatment. However, SLA treatments had effective effect on the surface roughness of the modified PEEK. The S_a values of the SLA

surface was 0.058 μm , 0.875 μm , 2.895 μm , 3.746 μm and 5.809 μm , respectively, which increased with the increase in the alumina grit size.

3.3 Surface wettability of the AE PEEK and the SLA PEEK

The surface wettability of the modified PEEK was characterized by the calculated surface energy from the contact angle measurements. As shown in Fig. 4(a) and 4(b), the surface wettability of the AE PEEK had a dramatic improvement with the increased etching time. After 90 min etching, the contact angle of the AE PEEK discs was significantly reduced from 76.20° to 18.66°, and the corresponding γ_s^p value of the samples also exhibited an increase from 14.23 $\text{mN}\cdot\text{m}^{-1}$ to 75.07 $\text{mN}\cdot\text{m}^{-1}$. The surface energies of the AE discs shown in Fig. 4(b) were calculated based on the contact angles in Fig. 4(a). No significant variation was observed among the dispersive components of the PEEK from AE-20 min to AE-90 min, which indicated that the increase in the polar component was mainly responsible for the increase in the total surface energy of the AE PEEK.

The water contact angles and surface energies of the SLA PEEK with four sizes of alumina grits were also presented in Fig. 4. As shown in Fig. 4(c) and 4(d), the increase in surface roughness barely affected the water contact angle and surface polar energy of SLA PEEK, and the substrates in the SLA group had an invariable contact angle of 47° and an invariable surface polar energy of 40 $\text{mN}\cdot\text{m}^{-1}$. Compared with the AE PEEK, therefore, the surface wettability of the SLA PEEK was poorer due to the rougher surface.

Especially to be mentioned, the water contact angle of the SL PEEK increased from 76.2° to 91.1° with the increase in surface roughness, as shown in Fig. 4(c), which can explain the poor adhesion between the BG-CH coatings and SL PEEK. The large water contact angle of the SL PEEK resulted in the poor spreading property of the surface, where the BG-CH coating could not spread completely over the substrate surface. Because of the poor contact, the coatings could not adhere on the SL surface and peeled off during the drying process. Therefore, increase the roughness of the PEEK substrates alone could not strengthen the bonding of the BG-CH coatings due to the poor spreading property of the surface. In other words, sufficient wettability of PEEK was necessary to obtain a robust adhesion of the BG-CH composite coatings.

3.4 Fracture resistance and adhesion strength of the BG-CH composite coatings on the AE PEEK and the SLA PEEK

Four-point bending test and pull-off test were performed to investigate the bonding strength of the modified PEEK. Although the pull-off test is a standard test and widely used to evaluate the bonding strength [44], four-point bending test is more appropriate in this case because it simulates the stress conditions of spinal implants in service (a combination of shear and tension) as closely as possible, while the samples in the pull-off test experience tensile stress only. Therefore, emphasis is placed on the fracture

resistance in this study and the fracture resistance of the BG-CH composite coatings on the AE PEEK and SLA PEEK was shown in Fig. 5. For the AE PEEK and SLA PEEK, these surface treatments always induced a strong increase in the fracture resistance compared to that of the untreated material.

In Fig. 5(a), the fracture resistance G_c of the AE PEEK increased to the peak value of $18 \text{ J}\cdot\text{m}^{-2}$ as the etching time increased to 30 min. When further extending the etching time to 90 min, the G_c values stabilized at $\sim 17 \text{ J}\cdot\text{m}^{-2}$. When the G_c value reached the maximum $18 \text{ J}\cdot\text{m}^{-2}$, the BG-CH composite coatings on the AE-30 min PEEK had an adhesion strength σ of $3.35 \pm 0.46 \text{ MPa}$ by the pull-off test.

In Fig. 5(b), the G_c values of the SLA samples increased dramatically from $18 \text{ J}\cdot\text{m}^{-2}$ to $67 \text{ J}\cdot\text{m}^{-2}$, with an increase in the grit size from $240 \text{ }\mu\text{m}$ to $1190 \text{ }\mu\text{m}$. It was suggested that the increase in surface roughness effectively increased the bonding strength of the BG-CH composite coatings. With the maximum fracture resistance of $67 \text{ J}\cdot\text{m}^{-2}$, the BG-CH composite coating on the SLA- $1190 \text{ }\mu\text{m}$ achieved an adhesion strength of $5.73 \pm 0.86 \text{ MPa}$. Despite the different test method, the trends by tensile test were quite like the results in the four-point bending test. Both the fracture resistance and the adhesion strength of the BG-CH composite coatings on the SLA PEEK were much higher than those on the AE PEEK substrates. Besides, although the validity of adhesion strength for the bioactive coatings (e.g. HA) on PEEK for spinal implants was in dispute [8, 10], the maximum 5.73 MPa of the BG-CH coatings on SLA PEEK was higher than the previously reported 2.8 MPa for plasma-sprayed HA coatings on PEEK [9].

Typical micrographs of fractured interface of the BG-CH coatings on the AE-30 min PEEK and SLA- $1190 \text{ }\mu\text{m}$ PEEK after the four-point bending test were also shown in Fig. 6. The fracture surfaces of the two samples exhibited the similar mixed mode of failure (coating/coating and coating/substrate). Both the PEEK substrate and the BG-CH composite coating were observed on the fractured surface, indicating the complex crack propagation path along the initial notch to the interface of the composite coating and PEEK. In fact, the interface between the BG-CH composite coating and the PEEK substrate played a major role in the crack propagation since the residual coating left on the failure surface was small. The residual coating with small occupation on the rugged crack faces was the evidence of the crack propagating into the composite coating side due to the intrinsic flaws, such as micro-pores and micro-cracks within the coatings [46, 47].

3.5 In vitro bioactivity and cell response

Both the in vitro bioactivity in SBF and ALP activity of the BG-CH coated PEEK indicated significant improvement in the osteointegration of PEEK, as shown in Fig. 7. The in vitro bone bioactivity of the BG-CH coatings was evaluated by immersing the specimens in SBF solution for up to 14 days. As shown in Fig. 7(a), apatite crystals formed on the surface of the BG-CH coatings after immersion for only 1 day. The density of the apatite

layer increased with increasing immersion period up to 14 days. Fig. 7(b) illustrated the FT-IR spectra of the samples soaked in SBF for different durations. The vibration peak 570 cm^{-1} was the amorphous P-O peak of the BG particles in the unreacted coatings. After exposed in SBF for 1 day, it was replaced by the small bending vibration peaks of crystalline P-O (566 cm^{-1} , 602 cm^{-1}), indicating the presence of apatite layers. After 3 days, the vibration band intensity for carbonate (873 cm^{-1} , 1420 cm^{-1} and 1460 cm^{-1}) and crystalline P-O (566 cm^{-1} , 602 cm^{-1} , 960 cm^{-1}) increased with the increase of the immersion time, which was in accordance with the SEM analysis. The presence of PO_4^{3-} and CO_3^{2-} showed that the formed apatite layer on the BG-CH coatings was carbonated hydroxyapatite (CHA) [48]. The peaks at $1200\text{--}1080$ (broad), 800 and 459 cm^{-1} represented the network of Si-O-Si of the BG particles [49]. Fig. 7(c) shows the ALP activities of the MC3T3-E1 cells on the coatings. As compared with the uncoated PEEK substrate, the BG-CH-coated PEEK showed a significantly higher ALP level after 7 days and 14 days ($P < 0.001$).

The in vitro cell responses (cell adhesion and cell proliferation) of the BG-CH coating on PEEK also evidenced the biocompatibility of MC3T3-E1 cells compared with that of the uncoated PEEK substrate. After 24 h of culture, no morphological differences were observed between the cells on the PEEK and on BG-CH-coated PEEK samples (see Fig. A.1 in Appendix A). Cell proliferation measured by CKK-8 assay indicated a better cell proliferation of the BG-CH-coated PEEK than that of the uncoated PEEK on day 1 (see Fig. A.2 in Appendix A).

4 DISCUSSION

In this study, a robust and bioactive BG-CH composite coating on the modified PEEK was prepared by a dip coating method. Except the PEEK treated by sand blasting (SL), there were two surface conditions of PEEK created by acid etching (AE) and a combination of sand blasting and acid etching (SLA), where the BG-CH composite coatings could adhere with solid. The PEEK in the AE group had similar surface roughness with different surface wettability, while PEEK in the SLA group had similar surface wettability with different surface roughness. Therefore, the fracture resistance G_c of the BG-CH composite coatings on the AE PEEK and SLA PEEK were plotted as a function of the polar surface energy (γ_s^p) and surface roughness (S_a) respectively, as shown in Fig. 8. However, the fracture resistance and adhesion strength of the composite coatings were effectively enhanced by the surface roughness rather than the surface polar energy.

In Fig. 8(a), the fracture resistance G_c of the BG-CH coatings on the AE PEEK increased as the polar surface energy increased. The linear relationship between the G_c value and γ_s^p suggested that the γ_s^p primarily contributed to the adhesion of the BG-CH composite coatings on the AE PEEK [50, 51], considering the negligible surface roughness variation. The G_c approached the maximum of $18\text{ J}\cdot\text{m}^{-2}$ when the γ_s^p

component was about $70 \text{ mN}\cdot\text{m}^{-1}$ after 30 min etching.

Specifically, the increase in the polar component was probably due to the formation of oxyl functional groups on the substrate as analyzed by XPS in Fig. 9. The shape of the C 1s peak in Fig. 9(a) of the AE-90 min PEEK was like that of the raw PEEK, but the occurrence of carbonyl (C=O) groups indicated an increase in oxygen content. The shape of the O 1s peak in Fig. 9(b) of the AE PEEK differed from that of the raw PEEK, where the C=O peak at 532 eV increased as a result of the acid oxidation [52]. Furthermore, it was more likely that the wide O 1s peak was the sum up of several smaller peaks attributed to the formation of a variety of oxygen-containing functional groups, such as C-OH, COOH or COOR, during the acid etching [53, 54]. As confirmed by the XPS spectra and the contact angle measurements, the AE PEEK surface became more hydrophilic, which was beneficial to the wetting and spreading of the BG-CH composite solution [15, 50, 55]. In addition, the oxyl groups created on the etched substrate may favor the formation of the chemical interactions between the BG-CH coatings and the AE PEEK and contribute to the adhesion. As reported, the presence of a low concentration of polar groups (1%) can lead to a significant improvement of the adhesion strength of a joint [56]. In this study, as the polar surface energy increased, the interface fracture energy enhanced because the interface crack motion was resisted by the increase of chemical interactions [21, 57, 58]. Therefore, the chemical interactions between the AE PEEK surface and the BG-CH composite coating was responsible for the increased bonding and interface fracture resistance.

Fig. 8(b) presents the relationship between the G_c of the BG-CH composite coatings on the SLA PEEK substrate and the surface roughness of the substrate. With the increase in the surface roughness of SLA PEEK from $0.87 \mu\text{m}$ to $5.80 \mu\text{m}$, the fracture resistance G_c increased dramatically from $18 \text{ J}\cdot\text{m}^{-2}$ to $67 \text{ J}\cdot\text{m}^{-2}$. In comparison with the fracture resistance of the AE samples, the obvious increase in the G_c value after SLA treatment revealed a significant influence of the substrate roughness rather than the surface energy on the interface fracture resistance of the BG-CH coatings on PEEK.

In fact, the adhesion strength was measured by the pull-off test, which was designed to analyze mode I fracture and the four-point bending test was used to analyze the mixed mode fracture as shown in Fig. 10. The extra mode II fracture in the bending test generates the shear displacement in the initial stage of the crack formation, contributing to the increase in the interface fracture energy [40, 59, 60]. Subject to the shear and opening displacements along the crack surface, the interface fracture resistance between the BG-CH composite coatings on the SLA PEEK is influenced by the phase angle of loading and by non-planarity (roughness) of the interface [40, 61]. Especially at large phase angle, rough interface contributes to the crack motion resist by means of additional friction work and crack shielding and thereby modify the interface fracture resistance. The roughness-related shielding is manifested in a parameter α_0 , which is dependent on the wavelength of the rough interface [61]. In this study, the phase angle is about 52° and $\alpha_0 \geq 10$, whose calculations are in Appendix B and C [61, 62]. As the surface roughness

of the SLA PEEK was significantly increased, the material parameter α_0 exploded and contributed to the increase in interface fracture resistance between the BG-CH composite coatings on the SLA PEEK.

As shown in Fig. 10, it is inferred that the fracture energy of the interfaces measured at mixed mode stress came mainly from the chemical bonding between AE PEEK surface and BG-CH coating, while for the SLA PEEK, the main contribution of the increase in fracture resistance was from the crack shielding and dissipation due to the interfacial roughness. The increase in the adhesion strength under mode I stress measured by pull-off test was smaller than that in the fracture resistance, which indicated surface roughness variations were more pronounced in the interface fracture process at a mixed mode loading.

5 CONCLUSIONS

Robust BG-CH composite coatings have been prepared on PEEK by using dip coating method, in which the PEEK surfaces were modified after a combination of sand blasting and acid etching treatment (SLA). Sufficient wettability of PEEK was necessary for the adhesion of the BG-CH composite coatings. The bonding behavior of the BG-CH composite coating on the desirable wetting PEEK was effectively enhanced by the surface roughness rather than the surface polar energy. As the surface roughness of PEEK increased, the fracture resistance measured by the four-point bending test increased dramatically over $50 \text{ J}\cdot\text{m}^{-2}$. Pull-off test was also used to measure the adhesion strength of the coatings, but variations of the interface roughness were more sensitive in the fracture energy at the mixed stress mode in the four-point bending test. Furthermore, the BG-CH composite coated PEEK showed good bioactivity and in vitro cellular response. In conclusion, bioactive and well-adhered BG-CH coatings with good biocompatibility on SLA PEEK would be prospectively used for spinal or other orthopedic applications.

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SUPPORTING INFORMATION

Appendix A

Morphologies of MC3T3-E1 adhered on surface of (a) PEEK and (b) BG-CH-coated

PEEK samples after 24 h of culture (Fig. A.1), proliferations of the MC3T3-E1 cells cultured on the PEEK and the BG-CH-coated PEEK for 1 day, 3 days and 5 days by CCK-8 assay (Fig. A.2).

Appendix B

The calculations of phase angle of the samples under four-point bending test.

Appendix C

The calculations of roughness-related shielding parameter of the samples under four-point bending test.

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Figure captions

Fig. 1 Schematic of the four-point bending test. Representative dimensions: thickness of the substrate $h = 2.0$ mm, width of the substrate $b = 4.0$ mm, distance between the inner and outer pins $l = 10.0$ mm. The thickness of the coating layers was in the order of several micrometers.

Fig. 2 SEM micrographs of the surfaces (a) (d) and the cross sections (b) (c) (e) (f) of the BG-CH composite coatings on the AE and SLA PEEK substrates. The top (a-c) and bottom (d-f) pictures correspond to the coatings on the AE-30 min PEEK and SLA-1190 μm PEEK, respectively.

Fig. 3 The 3D profile images and surface roughness values of the PEEK substrates: (a) the raw surface, (b) the AE-30 min PEEK, (c) SLA-124 μm PEEK, (d) SLA-250 μm PEEK, (e) SLA-590 μm PEEK and (f) SLA-1190 μm PEEK, respectively.

Fig. 4 (a) Contact angles and (b) surface energies of the AE PEEK after different durations of acid etching; (c) water contact angles of the SL PEEK and SLA PEEK after sand blasting with alumina grits of four average sizes: 124 μm , 250 μm , 590 μm and 1190 μm ; (d) surface energies of the SLA PEEK, where γ_s^p , γ_s^d and γ_s represents the surface energy polar component, disperse component and total surface energy of the PEEK, respectively.

Fig. 5 (a) Effects of etching time on the fracture resistance of the BG-CH composite coatings on the AE PEEK and the adhesion strength of the AE-30 min PEEK samples; (b) effects of grit particle size on the fracture resistance of the BG-CH coatings on the SLA PEEK and the adhesion strength of the SLA-1190 μm samples.

Fig. 6 SEM micrographs of the fractured BG-CH composite coatings on the (a) AE-30 min PEEK and (b) SLA-1190 μm PEEK substrate after four-point bending test.

Fig. 7 (a) SEM images of the BG-CH-coated PEEK after being soaked in SBF for different periods: (a1) 1 day, (a2) 3 days, (a3) 7 days and (a4) 14 days; (b) FT-IR spectra of the BG-CH coated PEEK before and after exposed in SBF; (c) alkaline phosphatase activity of the MC3T3-E1 cells cultured in the extract liquids of the uncoated PEEK and the BG-CH coated PEEK for 3, 7 and 14 days.

Fig. 8 (a) The fracture resistance (G_c) of the BG-CH coatings on AE PEEK as a function of the surface polar surface energy, with the adhesion strength (3.35 MPa) where the

maximum G_c was $18 \text{ J}\cdot\text{m}^{-2}$; (b) the fracture resistance (G_c) of the BG-CH coatings on SLA PEEK as a function of the surface roughness, with the adhesion strength (5.73 MPa) where the maximum G_c was $67 \text{ J}\cdot\text{m}^{-2}$.

Fig. 9 C 1s spectra (a) and O 1s spectra (b) of the raw PEEK substrate and the AE-90 min PEEK substrate. The relative intensities of the functional groups were calculated based on data from the XPS higher resolution spectra.

Fig. 10 The proposed adhesion mechanism of the BG-CH composite coatings on the (a) AE PEEK substrates and (b) SLA PEEK substrates; and different stress mode of coatings under (c) pull-off test and (d) four-point bending test.

(a) Surface polar energy

Chemical bonding

(b) Surface roughness

Chemical bonding + friction

(c) Pull-off test

(d) Four-point bending test

Table 1

Different surface treatments of the PEEK discs

Groups	Treatment method	Parameters
Controlled group	No treatment	--
1	Sand blasting (SL)	Sand blasted with 124 μm , 250 μm , 590 μm and 1190 μm alumina grits at a pressure of 30 bar.
2	Acid etching (AE)	Etching time: 10, 20, 30, 60 and 90 min.
3	A combination of sand blasting and acid etching (SLA)	Sand blasted with 124 μm , 250 μm , 590 μm and 1190 μm alumina grits, respectively. Then all the blasted surfaces were chemically etched for 30 min.

Graphical abstract

Highlights

- Bioactive glass-chitosan composite coating achieved a promoted adhesion after PEEK was modified by sand blasting and chemical etching.
- Four-point bending test and pull-off test were conducted to evaluate the bonding behavior.
- Hydroxyl groups on the PEEK surface contributed to the enhanced chemical interactions.
- Microscopic roughness was more pronounced in the fracture resistance improvement.