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Bioactivity and antibacterial effect of nitrogen plasma immersion ion implantation on polyetheretherketone

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ABSTRACT

Objective. We aimed to investigate the bioactivity and antibacterial effect of nitrogen plasma immersion ion implantation (PIII) on polyetheretherketone (PEEK).

Methods. According to the different modified parameters, the PEEK specimens were randomly divided into four main groups ($n = 49$/group): PEEK-C, PEEK-I, PEEK-L, and PEEK-H. Then, N_2-PIII surface modification was conducted using the corresponding parameters. The microstructure and composition of the modified PEEK surface was observed by scanning electron microscope (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The water contact angle of the PEEK surface was also studied by contact angle meters. The bioactive ability of PEEK samples was evaluated by observing the attachment, proliferation, and differentiation of MG63 cells cultured on the PEEK samples. Antibacterial property of the samples against *Staphylococcus aureus* was detected with the plate colony-counting methods.

Results. SEM and AFM analysis shows that PEEK-C surface is relatively smooth with the Ra value of 50.6 ± 2.52 nm. PEEK-I and PEEK-L surface is rough with the Ra value of 435.9 ± 6.47 nm and 443.23 ± 5.49 nm, respectively, and the PEEK-H surface is the most rough with the Ra value of 608.4 ± 3.14 nm. XPS element analysis demonstrated that nitrogen functional groups were successfully introduced into the surface of PIII-modified PEEK. Biological evaluation and the antibacterial results showed that nitrogen PIII treatment can significantly improve the biological activity of PEEK, and samples showed antibacterial properties against *S. aureus*.

Significance. PEEK surface subjected to the N_2-PIII treatment showed better biological activity and antibacterial effect. Therefore, N_2-PIII-treated PEEK surface is promising in bone tissue engineering and dental applications.

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1. Introduction

In recent years, with the continuous increase in the proportion of aged population, dentition defect in patients is increasing year by year. Therefore, the demand for dental implanted materials is also very strong. Due to the increasing number of bone defects caused by trauma, infection, tumor resection, and other conditions such as craniotomy, the patient's health faces serious threats. Pure titanium, as the most commonly used medical implant material, especially oral implant material, has achieved good clinical effect: it not only successfully helps countless patients with bone defect to receive the ideal morphology, it also objectively promotes the popularization and development of the concept of oral implant. Due to elastic modulus mismatch between titanium implant material and the surrounding bone tissue. When titanium was implanted in vivo, stress peaks at the bone implant interface could occur, causing an overload of peri-implant bone and therefore bone loss. Which is the so-called "stress shielding effect", eventually leading to loosening of the implants [1]. Some patients using titanium metal undergo allergic reactions [2], and thin gingival biotype with titanium implants possess easily exposed metal color, thus having aesthetic impact. To overcome these problems and to reduce adverse biological effects after implantation, looking for new alternative materials is very important.

Polyetheretherketone (PEEK), a high-performance metal-free medical implant material, has been used in the clinic with the authorization from the US Food and Drug Administration (FDA). As a semi-crystalline aromatic organic polymer compound, the melting point of PEEK can reach up to 335 °C. Compared with titanium, the biggest advantage of PEEK used as implant material in orthopedics is that it has similar elastic modulus (3–4 GPa) as the cortical bone [3]. And this can reduce the "stress-shielding effect" that can be seen in titanium-based implants [4]. Therefore, PEEK can be considered a promising metal-free prosthesis biomaterial for implantation. In the field of oral medicine, PEEK and its composites are mainly used as temporary abutments of implants, as orthodontic bite bar, in orthodontic aesthetics, and in fixed clamping rings [5–8]. In the field of orthopedics, PEEK and its composites are mainly used in spinal surgery, joint surgery, wound healing, and other fields, which has achieved satisfactory repairing effect [2,9]. However, the biological activity of PEEK is very poor because of its inert surface. When used as dental implant or bone defect repair material, it is difficult to obtain optimal osseointegration effect [10]. This is also the reason why PEEK has not been used widely in clinical applications.

Confronted with the critical issue that the PEEK surface does not show biological activity, resulting from its high chemical inertness, current research has focused mainly on two aspects: the preparation of PEEK composites and surface modification. The preparation of PEEK composites could be achieved by the method of blending active substances, such as preparing TiO_2/PEEK composites by blending TiO_2 [11], preparing hydroxyapatite (HA)/PEEK composite by blending HA [12,13], preparing FA/PEEK composite by blending nano-fluorapatite [14,15]. Surface modification mainly accomplished by chemical etching [10,16], surface coating [17,18], plasma surface treatment [19–21]. The modified strategies mentioned above can improve the biological activity of PEEK to a certain extent. However, chemical etching can result in reduced mechanical strength [16]. The surface coating is easy to be degraded in the body fluid environment because of low crystallinity [22]. There is also the risk of stripping due to thermal expansion coefficient mismatch between coating and matrix [23]. Surface modification layer obtained by plasma surface treatment is thin, which is often unable to meet the properties required to be used as medical implant material [24].

Plasma Immersion Ion Implantation (PIII) is a novel surface modification method, which can change the surface microstructure and chemical composition of polymeric materials without affecting their bulk properties [25]. Moreover, the treatment is not only easy to conduct but also highly efficient. The corresponding elements and chemical groups can be introduced into the surface of PEEK by different plasma injection sources [26–28]. Previous studies have shown that nitrogen-containing functional groups can be introduced on the surface of polymer materials by nitrogen PIII, and the resulting surface exhibits osteogenic activity and antibacterial properties [29,30].

As a linear aromatic macromolecule, the surface structure and composition of PEEK can be changed after being bombarded by high-energy plasma particles. Wang et al. reported that many "ravined structures" and hydroxyl groups are constructed on water-PIII-treated PEEK surfaces, which were favorable for the adhesion and proliferation of osteoblast precursor cells MC3T3-E1 [26]. Similarly, the PEEK surface also can be modified with the formation of hydrophilic nanostructures using titanium PIII. The obtained surface layer promoted the adhesion, proliferation, and osteoblast differentiation of cells cultured on PEEK surface [26,27,31].

The aim of this present study was to investigate the bioactivity and antibacterial effect of nitrogen PIII modification on PEEK. Finally, we lay a foundation for their widespread clinical application of PEEK and its composites in the field of dental implant, bone defect repair and joint replacement.

2. Materials and methods

2.1. *Sample preparation*

A total of 196 biomedical grade disk PEEK standard samples (Jilin University Super Engineering Plastics Research Co., Ltd., China), with dimensions of 10 mm diameter and 1 mm thickness, were prepared. Prior to surface treatment, all samples were ground with 600-, 800-, 1000-, and 1200-grit silicon carbide abrasive papers, as well as diamond paste to achieve a near mirror finish. Then, they were ultrasonically cleaned using acetone, ethanol, and deionized water in an ultrasonic water bath (Euronda, Italy) for 10 min. After air-drying carefully, all samples were randomly divided into the PEEK-C and the N_2-PIII-treated group. Then, all samples of the PIII-treated group were modified in the PIII device (Harbin Institute of Technology, Harbin, China). The schematic of N_2-PIII modification on PEEK is illustrated in Fig. 1. According to the different