Exploration on Surface Modification of Frontier Materials in Stomatology

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***Abstract*—Purpose: To investigate the effect of low temperature plasma treatment of ammonia on the bonding strength of PEEK and the mechanism of improving the bonding performance. Method: According to different modification parameters, the prepared pure PEEK standard samples were subjected to low-temperature plasma surface treatment of ammonia gas at 0, 10, 20 and 30min respectively (control group, plasma 10, 20 and 30min group), with 4 samples in each group. Specimens are observed by a scanning electron microscope (SEM) after processing the surface microstructure change, adhesive bonding specimen preparation for 21% Scotchbond Universal Adhesive (3M ESPE), 37 ℃ water bath after 24 h testing shear strength of the specimens, stereoscopic microscope each failure mode. Result: After the treatment of ammonia plasma at low temperature, the surface of each group of specimens became uneven. The results of X-ray photoelectron spectroscopy (XPS) showed that nitrogen was introduced into the surface of the modified materials. The shear strength of the specimens after plasma treatment was significantly higher than that of the control group (p<0.01), and the shear strength of the 20min plasma group was higher than that of the 10min and 30min groups, with statistically significant differences (p<0.01). The shear strength of the 30min plasma group was higher than that of the 10min plasma group, with statistically significant differences (p<0.01).The failure modes of the specimens in each group were mainly interface failure. Conclusion: low temperature plasma treatment with ammonia gas can significantly improve the adhesion strength of PEEK oral biomaterial, and the 20min treatment group was the best.**

***Index Terms*—PEEK (polyether-ether-ketone); ammonia gas; low temperature plasma; surface energy**

I. Introduction

Polyetheretherketone (PEEK) is a polymer compound first developed by the British imperial chemical industry group in 1978. PEEK has good physical and chemical properties, such as high mechanical strength [1], wear resistance [2], corrosion resistance, X-ray penetration, low density, good biocompatibility [3] and potential bacteriostatic properties [4,5]. PEEK good mechanics performance in: high tensile strong degree and breaking strength, especially importantly, PEEK of elastic modulus for 3 ~ 4 GPa, the use of titanium and titanium alloy material than usual (modulus of elasticity is about 110 GPa) is closer to human bone dense qualitative elastic modulus (about 14 GPa), similar to human bone dense mass of elastic modulus of the PEEK can effectively avoid bone absorption caused by stress shielding. PEEK thus became an important bone replacement material in the medical field [6]. Due to its advantages of nonmetal color, low weight, high strength, so the PEEK can be used for fixed denture or activity denture [7,8], studies have found that [7], PEEK base fixed bridge restoration fracture strength can reach an average of 1383 N, higher than that of Behr etc. [9] reported tooth of the area before restoration should be able to withstand 300 N, the teeth area of about 500 ~ 600 N force. PEEK grey color, single, not fully disadvantages limit its clinical application, such as finishing resin can improve the PEEK this defect, but PEEK is a kind of biological inert material, and resistance to surface modification, its combined with composite resin, interface bonding strength is low, and the composite resin is difficult to build a strong and lasting bond [10]. Therefore, improving PEEK's surface performance has become a hot research topic. This experiment mainly studied the influence of low-temperature ammonia plasma treatment on PEEK and 21% Scotchbond Universal Adhesive (3M ESPE) shear strength, so as to further understand the adhesive properties of PEEK biomaterials and provide theoretical basis for the clinical application of PEEK biomaterials in the oral field.

II. Materials and Methods

A. Materials and Main Equipment

PEEK (changchun jida plastic engineering research co., LTD., China), 21% Scotchbond Universal Adhesive (3M ESPE), (3 m, the United States), plasma generator (nanjing Mr Company, China), the universal mechanical testing machine (5869 50 kn, INSTRON company, USA), stereoscopic microscope (SZX16, push around, Japan), field emission scanning electron microscopy (SEM, S - 4800, the United States), X-ray photoelectron spectrometer (ESCALAB 250, Thermo company, USA), Injection molding machine (SZ15, Shanghai special radio machinery factory, China), ultrasonic cleaning machine (EURONDA, Italy)

B. Specimen Preparation and Grouping

First, the injection molding technology preparation of 16 PEEK standard specimen (60 mm × 6 mm × 5 mm), the 500 #, 900 # water sand paper burnish, step by step and with acetone, ethanol and deionized water ultrasonic cleaning every 15 min after the air gun to blow dry preparation of standard of 16 specimens were randomly divided into control group and experimental group, the experimental specimen put in plasma generator, according to the different processing parameters are divided into plasma 10, 20 and 30 min group, processing parameters of each specimen are shown in table 1.

Table 1. Plasma processing parameters.

Group	Voltage (V)	Frequence (Hz)	Pressure (Pa)	Gas velocity (sccm)	Time (min)	Power (W)
control group	-	-	-	-	-	-
Plasma 10min group	500	13.56	20	20	10	500
Plasma 20mingroup	500	13.56	20	20	20	500
Plasma 30min group	500	13.56	20	20	30	500

“ - ” : No data.

C. *Characterization*

The specimens of each group were adhered to the loading platform with conductive adhesive, the microscopic morphology of the specimens of each group was observed by electron microscope (SEM), and the element composition changes on the surface of the materials of each group were analyzed by X-ray photoelectron spectroscopy (XPS).

D. *Preparation of Bonding Specimens*

Firstly, double-sided tape with circular holes (diameter: 1.8 mm) is pasted on the surface of the specimens, and 5 bonding specimens are prepared on each specimen. Place a 5 mm high cylindrical polyethylene mold with an internal diameter of 1.8 mm on a circular hole of double-sided tape, fill the mold with RelyX TM Unicem resin binder, cure 50 s LED light, and place the mold at room temperature for 40min before gently removing the mold. The preparation of the adhesive specimens were placed in 37 ℃ water bath, constant temperature storage for 24 h.

E. *Measuring Shear Strength*

Use the universal mechanical testing machine to shear strength test samples, with special fixture fixed sample, shear loading head close to the PEEK and resin adhesive bonding surface, shear direction parallel to the bonding surface, loading rate of 1 mm min - 1, loading direction is vertical load, until the sample 21% Scotchbond Universal Adhesive (3M ESPE), record at this time of the shear stress value (F), according to the formula: shear strength (T) = maximum load shear force (F)/area (S). The fracture interface of all tested samples was observed with a stereoscopic microscope (40 times magnification) to evaluate the failure mode. If the broken end is on the bonding interface between PEEK and 21% Scotchbond Universal Adhesive (3M ESPE), it will appear as interface failure. If the broken end of the specimen is inside the resin binder or inside the specimen, it shows cohesion failure. A small amount of resin adhesion, that is, the interface failure and cohesion failure exist at the same time, is shown as mixed failure.

F. *Statistical Analysis*

Using SPSS 22.0 software to statistical analysis of data, shear strength in the form of X + S said, Univariate anova was used for comparison between groups, and LSD method was used for difference comparison.

III. THE RESULTS

A. *SEM Observation*

Figure 1 shows the SEM morphology of PEEK samples in each group. Among them, PEEK in the control group had a relatively flat surface and only a few irregular fine lines after being polished by no. 900 water-sand paper. After ammonia gas low-temperature plasma treatment, the surface of the material becomes uneven, and with the extension of treatment time, the etching effect becomes more and more obvious.

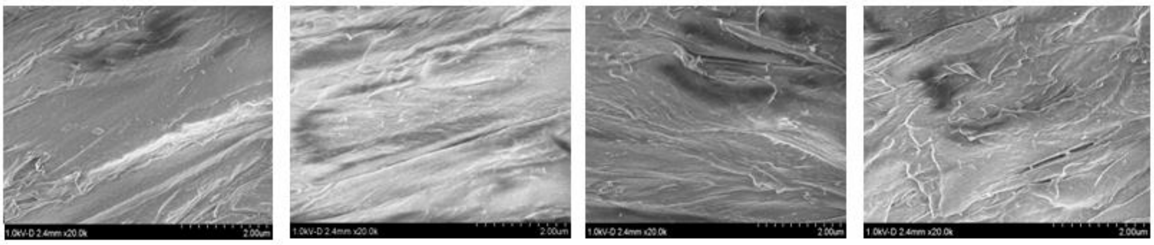

Figure 1. PEEK specimen surface morphology after ammonia plasma treatment (×1000 times).

A: control group B: plasma 10min group C: plasma 20min group D: plasma 30min group

B. *XPS Elemental Analysis*

Figure 2 shows the surface elemental analysis results of PEEK samples in each group. As can be seen from figure 2, PEEK in the control group mainly contained C and O elements, while N elements were successfully introduced into the material surface after ammonia plasma treatment, forming the structure of nitrogen-containing organic functional groups. This may be because plasma bombarding PEEK substrate led to the break of its polymer chain and formed new chemical bonds with nitrogen plasma at the same time.

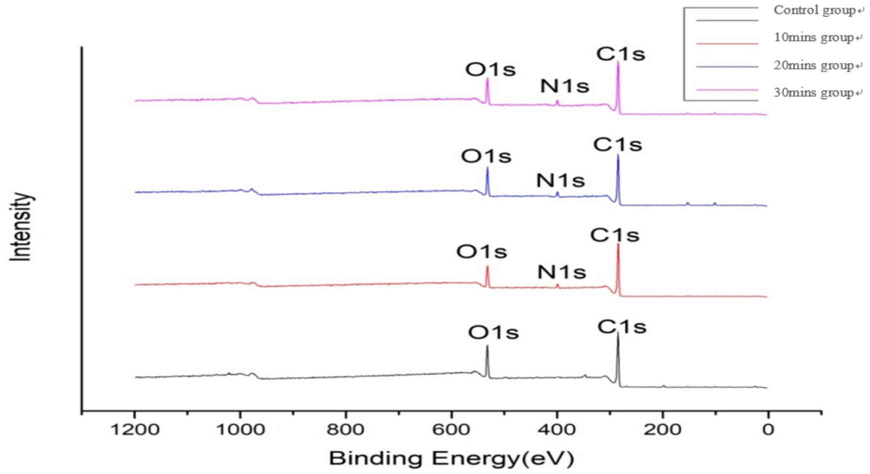

Figure 2. XPS elemental analysis full spectrum of PEEK samples in each group.

C. Shear Strength Value and Bond Interface Failure Mode

PEEK (control group) without ammonia plasma treatment hardly bonded with 21% Scotchbond Universal Adhesive (3M ESPE), and the shear strength of the specimens after plasma treatment was significantly higher than that of the control group. After 10min of cryogenic nitrogen plasma treatment, the shear strength value (5.46 +/- 1.35) was significantly higher than that of the control group (0), and the difference was statistically significant ($p<0.01$).Compared with the plasma group of 20 min, the shear strength value of the specimens in the plasma group of 30 min (9.18 +/- 1.77) was also significantly increased, and the difference was statistically significant ($p<0.01$).Compared with the plasma group of 20 min, the shear strength of the specimens in the plasma group of 30 min (6.03 +/- 1.01) decreased, and the difference was statistically significant ($p<0.01$). However, the shear strength of the specimens in the 30 min group was still higher than that in the 10 min group, and the difference was statistically significant ($p<0.01$), as shown in table 2. The bonding failure mode of each group of specimens is mainly interface failure, as shown in table 3.

Table 2. Shear strength of each group of specimens after different surface treatments (n = 20).

Group	**Shear strength** (MPa, X ± S)
control group	0^{a}
Plasma 10min group	5.46 ± 1.35^{b}
Plasma 20min group	9.28 ± 1.77^{c}
Plasma 30min group	6.03 ± 1.01^{d}

Note: a, b, c and d indicate statistical differences between different groups ($p<0.01$).

Table 3. Bonding failure modes after different surface treatments (n = 20).

Group	**Failure mode**		
	Interface damage	Cohesive failure	Mixed destruction
control group	—	—	—
Plasma 10min group	17	0	3
Plasma 20min group	18	0	2
Plasma 30min group	16	0	4

“ - ” : No data.

IV. Discussion

As a surface hydrophobic material, PEEK has insufficient bonding strength with resin, which limits its application in stomatology [11]. For this reason, researchers have used various methods to improve its surface energy.

Plasma modification is a widely used surface modification technology in the field of polymer materials [12,13]. After treated with low temperature plasma material surface, materials of nonpolar surfaces into polar surface, the effect of the material surface plasma bombardment may include: micro etching to produce rough surface, surface activation, the formation of a surface crosslinking layer, removal of organic residue, etc., all of which can increase the bonding interaction, so as to improve adhesive performance, nitrogen, oxygen, argon, ammonia and other widely used in polymer materials of low temperature plasma surface treatment [14,15]. In order to improve the bonding performance of PEEK oral repair material, the group adopted the ammonia gas low temperature plasma treatment, ammonia plasma immersion ion implantation this method in addition to increasing PEEK surface roughness, and improve the material and adhesive between mechanical retention force, this method can improve the wettability on the surface of the PEEK, and processing after the introduction of new functional groups on the surface of can combine with binder composition in the form of chemical bonding force, to a certain extent, improve the bonding performance of the material [16].

In this study, PEEK was treated with ammonia plasma at low temperature. Due to the different processing time, the shear strength of PEEK was also different. On the one hand, too long plasma treatment time will destroy the active groups formed on the surface of the sample and reduce the number of polar groups. On the other hand, the surface roughness of the sample is related to the plasma treatment time. The longer the treatment time is, the more serious the surface etching is and the larger the surface roughness is [17]. The main component of 21% Scotchbond Universal Adhesive (3M ESPE) contains phosphate monomer, which is difficult to generate chemical bonding force with PEEK material, so the bond strength between 21% Scotchbond Universal Adhesive (3M ESPE) and PEEK is very weak [18]. In this experiment, 21% Scotchbond Universal Adhesive (3M ESPE) hardly bonds with PEEK in the control group, which also verifies this view. Compared with the control group, the shear strength of the specimen increased significantly after 10 min of plasma treatment, which was due to the introduction of active groups on the surface of the specimen after plasma treatment and the formation of cross-linking layer. The shear strength of the group treated with plasma for 20 min was significantly higher than that of the group treated with plasma for 10min, which was due to the fact that with the extension of the plasma treatment time, the surface etching of the sample was deepened, the roughness was increased, and the mechanical bonding played a significant role. However, the shear strength of the specimen decreased after 30 min treatment, which was due to the damage of the polar group with the extension of treatment time. It can be seen that chemical bonding and mechanical bonding play an important role in PEEK's bonding performance.

In order to quickly and effectively detect the adhesive properties of materials, testing the shear strength is a feasible method, because the shear strength is related to the chemical and mechanical bonding of the material surface, and any factor that can change the characteristics of the material surface will affect the size of the shear strength value. In this experiment, PEEK and 21% Scotchbond Universal Adhesive (3M ESPE) have low shear strength, and the main failure mode is interface failure, which verifies this view. The mixed failure in the experiment is caused by the uneven stress distribution at the interface.

V. Conclusion

Low temperature plasma treatment with ammonia gas can significantly enhance the bonding strength of Unicem resin binder and PEEK, and the bonding strength between the two is the highest when treated with plasma for 20min, thus providing a reference basis for PEEK's application in the oral cavity.

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