Preparation and Characterization of Composite Resin Containing Anion Powder

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Abstract. Objective. Anion powder is a kind of cyclic silicate mineral with antibacterial effect. A new type of composite resin containing anion powder was prepared by adding anion powder into the composite resin. Methods. By using mechanical mixing dispersion and ultrasonic dispersion, silane coupling agent was added, and the anion powder was evenly dispersed in Durafill (DF) composite resin at the proportions of 0, 1%, 2%, 4%, respectively. EDS was used to detect the relative content of anion powder in composite resin, and scanning electron microscope (SEM) was used to observe the dispersion uniformity of anion powder. The friction coefficient (COF) of composite resin containing anion powder was measured by UMT-2MT friction and wear tests. The influence of different proportion of anion powder added to the composite resin on its mechanical properties. The next step is to test the antimicrobial property of the composite resin containing anion powder, in order to find the best proportion of anion powder added to the resin. Results Mechanical agitation dispersion and ultrasonic dispersion were applied, silane coupling agent was added, and anion powder of different proportions was successfully mixed into the composite resin. EDS results showed that anion powder was successfully added into the composite resin, and the surface particles were uniformly dispersed by SEM. The friction and wear experiments showed that the addition of anion powder would change the mechanical properties of the composite resin, and the friction coefficient of the composite resin was higher than that of the control group, and the friction coefficient of the composite resin increased with the increase of anion powder content.

1. Introduction
With the development of dental materials, dental filling materials are also developing. From silver amalgam to glass ionomer cement and composite resin, they have been applied in clinic with their respective advantages. At present, the commonly used dental filling material is composite resin, which has good biological safety, good aesthetic effect and clinically acceptable mechanical properties, and is widely used in the repair of various dental defects [1]. In particular, its physical properties such as wear resistance is improved, and clinical dentists operate more conveniently, so the clinical application is more and more extensive.

However, after the repair of photosensitive composite resin, due to the failure of edge sealing, micro-leakage and secondary caries caused by saliva and microbial infiltration around the restoration body are common, which are the main factors leading to the failure of filling [2]. Clinically, the main reason for the loss of the prosthesis after filling is the formation of secondary caries around the material, and about 50 ~ 60% of the prosthesis replacement patients were diagnosed as secondary caries [3]. The long-term use of oral materials has always been the focus of clinicians, which is directly related to the quality of
tooth restoration. In recent years, the research and development of antimicrobial oral materials are gradually emerging. Scholars expect to inhibit the adhesion of pathogenic bacteria around oral materials by making the materials have antimicrobial properties, so as to extend the use time of oral materials and improve the repair efficiency [4].

Antimicrobial agents are divided into natural, organic, inorganic and organic polymer antibacterial agents. Inorganic antimicrobial materials have attracted more and more attention due to their excellent properties. Compared with ordinary materials, inorganic antimicrobial materials have the advantages of aging resistance, high temperature resistance, excellent comprehensive performance, stable antimicrobial property and long term [5]. At present, many scholars have paid attention to the addition of inorganic antibacterial agents into oral materials to make them have certain antibacterial properties, so as to reduce the generation of secondary caries after restoration and extend the service life of prosthesis [6].

Inorganic antibacterial agents can be divided into two categories according to the mechanism of their action on microorganisms. One is the combination of metal compounds with antibacterial effects (silver, copper, zinc, etc.) and inorganic carriers (such as zeolite, bentonite, activated carbon, etc.), which are called silver antibacterial agents [7]. The other is the use of photocatalytic substances as antibacterial agents, such as titanium oxide is a widely used photocatalyst, called titanium dioxide photocatalyst system antibacterial agent [8]. Silver, copper, zinc and other metal have antibacterial ability, through the methods of physical adsorption and ion exchange, the silver, copper, zinc and other metal ions (or its) fixed on the different carrier made of different types of silver antibacterial agent, including antibacterial zeolite antimicrobial agent, bentonite, silica gel antibacterial agent, phosphate double salt antibacterial agent, etc. [9].

Anion powder (Negative ions powder) is a kind of annular silicate minerals, composed of SiO$_2$, FeO, Fe$_2$O$_3$, B$_2$O$_3$, Al$_2$O$_3$, Na$_2$O, MgO style, Li$_2$O and MnO, contains trace Cr, Zr, zinc and Ti elements beneficial to human body, known as the vitamin in the air, can adjust the body from the balance between positive ion and negative ion, and can inhibit the aging of human body cell [10]. Zhang and others added the negative ions powder to the denture base resin, which showed that the mechanical properties of the composites increased with the increase of negative ion content [11,12]. Zhang cailing added tourmaline nano-powder and mint extract with hair generating anion function to viscose cellulose spinning solution, and the results showed that the fiber had good antibacterial and anion generating function [13].

Antibacterial composite resin refers to the addition of antibacterial agents in the composite resin, so that its own antibacterial, in a certain period will stick to the above bacteria to kill or inhibit its proliferation. It is generally required that the antimicrobial properties of composite resin products have high efficiency, wide spectrum, good continuity, non-toxic and odorless, and have good biocompatibility and mechanical properties [14]. At the same time, studies have shown that the addition of inorganic fillers into the matrix of composite resin can enhance its performance, reduce the volume change during polymerization, reduce the thermal expansion coefficient, inhibit deformation, improve resin rigidity, surface hardness and wear resistance and other mechanical properties [15]. Based on this, the preparation and characterization of the anion powder added to the photocurable composite resin have been completed in this paper. The next step is to carry out the antibacterial performance test.

2. Methods

2.1 Materials and equipment

2.1.1 Materials (Table 1)

| Name                  | Manufacturer                                      |
|-----------------------|---------------------------------------------------|
| Negative ions powder  | ultra - fine powder laboratory self-processing    |
| Anhydrous ethanol     | Li "an long bohua pharmaceutical chemical co., LTD |
Silane coupling agent | Tianjin chemical reagent co. LTD
---|---
N, n-dimethyl formamide (DMF) | Li ‘an long bohua pharmaceutical chemical co., LTD
High purity deionized water | Millipore, inc
DF light curing composite resin | Germany heraeus gusha dental co., LTD

### 2.1.2 Equipment (Table 2)

| Name                                      | Manufacturer                                      |
|-------------------------------------------|---------------------------------------------------|
| Scanning electron microscope             | SEM, JEOL, 5600, Louis vuitton, Japan             |
| Light curing machine                     | Dentsply                                          |
| Ultracentrifuge                          | Optima L-100XP, the United States                 |
| Microhardness tester                     | Hengyi precision instrument Co. LTD. China        |
| Fourier transform infrared spectrum      | ATR-FTIR, IFS66V/S, Bruker                        |
| Umt-2mt reciprocating friction meter     | CETR corporation, USA                             |

### 2.2 Prepare composite resin composites containing anionic powder

Anion powder dispersed in the resin matrix material by solution mixing method\(^{[16]}\), using anhydrous ethanol as solvent. In the process of mixing, this experiment adopts the method of mechanical stirring and ultrasonic dispersion to prevent particles together.

(1) In the experimental group, negative ion powder was added to the composite resin material in the proportion of 1%, 2% and 4%, respectively. 4g of each resin was taken and dissolved with anhydrous ethyl ether. A drop of silane coupling agent was added and mixed evenly with magnetic agitator and ultrasonic oscillation according to the above proportion. Finally, the rotatory evaporator was used to remove diethyl ether and different proportions of anionic powder composite resin were prepared.

(2) Control group: the composite resin sample without anion powder was 4g, and the composite resin without anion powder was prepared according to the same treatment method of the experimental group.

### 2.3 Scanning electron microscopy

The sample containing 0%, 1%, 2% and 4% anion powder was vertically irradiated by the photocuring machine at 500w·cm\(^{-2}\)·40s curing condition to make a plate-shaped solid block, which was sprayed with gold after surface polishing, and then the anion powder dispersion was observed by SEM.

### 2.4 EDS analysis of the relative content of Al and Si

The relative contents of Al and Si on the surface of the sample containing 0%, 1%, 2% and 4% anion powder were analyzed by electron energy spectrometer.

### 2.5 Mechanical performance test

The friction properties of composite resin materials containing anion powder were tested in accordance with international standard (ISO 4049-1978) and Chinese dental composite resin material standard (YY 91042-1999).

Preparation of friction test specimens: 20mm·10mm·1mm; Each group has three specimens, and the curing condition is the same as (1). Both ends of the specimen with 600 mesh water sand paper burnish, polishing, make the surface level, the specimens preserved in 37 ℃ physiological saline for 24 h after...
the test.

The friction performance: the configured artificial saliva was added into the container as the friction medium, take the steel ball as the grinding head, load 20 N, frequency 2 Hz, friction time 30 min, repeat the test for 3 times for each sample. The friction coefficient when the friction curve of each sample is stable is recorded and the average value is obtained.

2.6 Data statistics
SPSS10.0 data statistical analysis system software was used for one-way anova and t test.

3. Results and discussion

3.1 Scanning electron microscopy (SEM)
The results of scanning electron microscopy (SEM) on the surface of composite resin containing 0%, 1%, 2% and 4% anion powder are shown in Figure 1. Figure 1A shows no anionic particles in the control group. Figure 1B, C and D show that there are many cubic anion powders that have been mixed into the composite resin without agglomeration and dispersed well. The results show that the anion powder was successfully combined with the composite resin and the anion powder could be uniformly dispersed without agglomeration.

Figure 1. SEM images of anionic powder composite resin with different proportions (0%, 1%, 2%, 4%)

3.2 EDS
The composition of anion powder is shown in Table 3

| Composition | Content (wt %) |
|-------------|----------------|
| Al₂O₃        | 35.10          |
| The SiO₂     | 34.81          |
| B₂O₃         | 11.02          |
| MgO style    | 4.70           |
| Fe₂O₃        | 10.18          |
| Na₂O         | 0.91           |
| P₂O₅         | 0.22           |
| TiO₂         | 0.26           |

The relative contents of Al and Si elements on the surface of samples containing 0%, 1%, 2% and 4% anionic powder analyzed by EDS are shown in Table 4.
Table 4 Relative contents of Al and Si elements on the surface of anionic powder composite resin samples

|        | Al (weight %) | Si (weight %) |
|--------|--------------|--------------|
| 0      | 2.08         | 4.11         |
| 1%     | 10.25        | 9.32         |
| 2%     | 12.66        | 11.25        |
| 4%     | 15.05        | 14.11        |

It can be seen from Table 3 that the main composition of anion powder is Al₂O₃ and the SiO₂. EDS detection of composite resin containing anion powder was carried out accordingly. Table 4 showed that with the increase of the proportion of anion powder added, the relative content of Al and Si elements increased, indicating that anion powder had been successfully added into the composite resin.

3.3 Experimental results of friction and wear

![Figure 2](image_url)

Figure 2 shows the original data of friction coefficient of composite resin material containing anion powder and steel ball after grinding and its statistical analysis results. The figure shows the corresponding friction curve, showing the change trend of friction coefficient in the friction process with the friction and wear experiment. The experimental results showed that the friction coefficient of the anion powder changed after adding the composite resin in different proportions, which was higher than that of the control group. After statistical analysis, the friction coefficient of the 1%, 2% and 4% groups were statistically significant compared with that of the control group.

If appropriate concentration of inorganic filler can improve the mechanical properties of the composite resin, but excess can cause decline. The experiment needs to test the appropriate concentration of anion powder. The anion powder added in composite resin in the experiment influenced the mechanical performance. The reason may be that the particle surface combined with resin matrix molecules groups, which may affect the original packing and resin matrix in combination, whether the hypothesis is yet to be further research.

4. Conclusion

The experiment successfully compounds the different proportions of anion powder mixed into the composite resin by mechanical mixing dispersion and ultrasonic dispersion. EDS results showed that anion powder was successfully added into the composite resin, and the surface particles were uniformly dispersed by SEM. The friction test show that the friction coefficient increases with the increase of anion...
powder content. However, the appropriate concentration of anion powder needs to be further studied. In addition, its long-term antimicrobial properties need to be further studied.

References
[1] R. A. Azeem, N. M. Sureshbabu, Journal of Conservative Dentistry Jcd, 21(2018)
[2] S. Kubo, A. Kawasaki, Y. Hayashi, Dental Materials Journal, 30(2011)
[3] F. F. Demarco, K. Collares, F. H. Coelho-de-Souza, M. B. Correa, M. S. Cenci, R. R. Moraes, N. J.M. Opdam, Dental Materials, 31, 10 (2015)
[4] S. Sakuma, Anti-bacterial composite particles and anti-bacterial resin composition[J]. (2003)
[5] S. T. Khan, A. A. Al-Khedhairy, J. Musarrat, Journal of Nanoparticle Research, 17, 6(2015)
[6] S. Savas, E. Kucukyilmaz, E. U. Celik, M. Ates, J Oral Sci, 57, 4(2015)
[7] H. M. Lim, H. J. Park, Current Green Chemistry, 2(2015)
[8] S. T. Khan, A. A. Al-Khedhairy, J. Musarrat, Journal of Nanoparticle Research, 17, 6(2015)
[9] Q. H. Tran, V. Q. Nguyen, A. T. Le, Advances in Natural Sciences Nanoscience & Nanotechnology, 4, 3(2013)
[10] F. Wang, Stabilization and application of ultrafine anion powder[D]. Shenyang university of technology (2016)
[11] Y. Zhang, G. Gao, X. Gou, W. Liu, B. Liu, H. J. Wang, International Conference on Advanced Computer Science and Engineering (ACSE), (2014)
[12] M. Liu, X. Zhang, J. Zhang, Q. Zheng, B. Liu, IOP Conference Series: Materials Science and Engineering, 301 (2018)
[13] C. Zhang, Studies on fiber formation and properties of anion powder/mint extract/viscose cellulose blend [D]. Qingdao university (2009)
[14] M. Uchida, K. Miyake, Y. Kurihara, Antibacterial zeolite particles and antibacterial resin composition, 2013.
[15] Ding J. Abrasion resistance of inorganic filler modified hydroxy-terminated liquid nitrile rubber /epoxy-resin composites[J]. China Synthetic Rubber Industry, 2014.
[16] L. Zhang, Study on Microstructure and Tribological Properties of Plasma Nitriding Forged CoCrMo Alloy[J]. Lubrication Engineering, 2010.