Advances in Resin-Based Dental Composite Materials

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Abstract. With the continuous development of dental materials, traditional dental materials such as alloy materials and porcelain veneers with the shortcomings of insufficient mechanical properties, susceptibility to secondary damage caused by fracture during use, and poor biocompatibility are gradually being replaced by dental resin composites with better mechanical properties, lower cost, and higher biocompatibility. A dental composite is a kind of dental material, which is made of matrix resin, inorganic filler, initiator system, etc. In this paper, some antibacterial materials, stimuli-responsive materials, and self-healing materials are reviewed. For antibacterial materials, this article introduces composite materials containing natural antibacterial agents, organic synthetic antibacterial agents, and inorganic antibacterial agents respectively. For stimuli-responsive materials, this article mainly introduces composite materials that respond to pH changes. For self-healing materials, this paper introduces the composite materials containing self-healing microcapsules, and briefly summarizes the joint application of self-healing microcapsule composite materials and other modified materials. At the same time, the main development directions of dental composite materials at present are summarized and prospects are presented.

Keywords: Resin-based dental, antibacterial materials, stimuli-responsive materials, self-healing materials, dental composite.

1. Introduction

In recent years, oral diseases have seriously affected global human health and people's quality of life. Dental caries is one of the main oral diseases. It is mainly due to the damage of dental tissue caused by chronic erosion after bacterial infection and is characterized by a high incidence rate and wide distribution. In a survey conducted by the World Health Organization in November 2022, in 2019, an estimated 3.5 billion people worldwide were suffering from oral diseases, accounting for nearly half (45%) of the total population. The global prevalence rates of primary and permanent dental caries were 43% and 29%, respectively. Therefore, as society develops and the standard of living improves, people pay increasing attention to oral health, and the relationship between dental treatment and the public is also becoming increasingly close. At the same time, the demand for dental materials is increasing, and the requirements for selected dental materials are also becoming higher. The early dental restoration materials used include porcelain veneers, alloy materials, and composite materials, among which silver amalgam materials have been used by people for nearly 150 years since the early 20th century. However, there are disputes about the toxicity of silver amalgam materials. In addition, there are many problems with the hardness, service life, histocompatibility with the oral cavity, and aesthetic degree of silver amalgam materials in use. In the application of porcelain fused to metal repair materials, people have also gradually found their own limitations and shortcomings, such as poor impact load, uneven bite force quotient, poor biocompatibility, etc. In addition, the interface between porcelain fused to metal materials and adhesives is also affected by temperature changes, saliva, and pH changes, which limit their service life. With the continuous development of dental resin composites [1], people gradually realize that dental resin composites have enormous advantages such as easy operation, aesthetic practicality, and excellent mechanical properties. They are mainly composed of resin matrix, reinforcing filler, and initiator. Since the mid-19th century, the emergence of resin based dental materials has sparked a revolution in dental materials. Resin based dental materials have the advantages of having a dental appearance, being stable in the oral environment, and possessing excellent mechanical performance, making them widely used in dental restoration and treatment. However, the original resin based dental composites still have some defects, including a relatively high coefficient of thermal expansion, a relatively low resistance to wear, polymerization shrinkage, and secondary cavities brought on by a potential failure of the resin dentine interface [2]. In addition, the oral cavity is a harsh environment for dental materials. Bacteria can produce acid, causing demineralization of hard tissues, leading to direct and indirect repair failures. They can interfere with esterases in saliva, leading to the hydrolysis and degradation of dental resin adhesives [3], and forming biofilms on materials, leading to bacterial growth. Therefore, in order to further strengthen the properties and service life of resin based dental materials, developing dental materials with antibacterial activity, stimuli-responsive, and self-healing properties is the main goal of dental researchers and materials scientists. New resin based dental materials improve their original properties or endow them with new functions by introducing reinforcement and functional fillers, using colorless and low toxicity initiators, resulting in low shrinkage, biosafety, and excellent mechanical properties. This article will focus on introducing new resin based dental materials with antibacterial properties, stimuli-responsive properties, and self-healing properties.

2. Antibacterial materials

More than 600 different microbial species, such as bacteria, viruses, fungi, mycoplasma, and chlamydia, have been colonized in the human oral cavity. Some of them will breed on the surface of resin based dental materials and form biofilms, leading to the failure of the resin dentine interface and the drop of dental material, and even further infection of damaged teeth. Therefore, it is necessary to develop dental materials with antibacterial properties, typically achieved by adding silver or one or more antibiotics into the material. Small molecule antibacterial agents will slowly release and form an antibacterial environment around the dental material. Antibacterial agents are mainly divided into natural antibacterial agents, organic synthetic antibacterial agents, and inorganic antibacterial agents. It is a type of auxiliary agent with bactericidal or antibacterial functions, which refers to the substance that can be added to the material to give it antibacterial properties, which is the core of antibacterial materials. Antibacterial agents are highly sensitive chemical components to bacteria, which can kill microorganisms attached to the surface of materials through physical or chemical reactions. Antibacterial materials refer to various materials that have antibacterial properties after being treated with antibacterial agents. During use, the growth and reproduction of microorganisms can be inhibited by antibacterial materials that are harmful to the human body, life, and production environment. In recent years, the number of studies on antibacterial resin based dental materials has rapidly increased, and more and more modification methods have been discovered.

When polymethyl methacrylate (PMMA) is used as denture resin, the implanted PMMA based resin will occasionally deform and grow bacterial biofilm at the interface between the oral cavity and biomaterials due to the thermal instability and humid environment of the oral cavity. Therefore, in order to improve the shortcomings of PMMA resin in the application of dentures, Ozdemir et al. selected polyethylene amine (PEI) and silk fibroin (SF) to successfully prepare a new type of nanofiber pad with antibacterial and mechanical reinforcement functions by combining polystyrene (PS), PEI and PMMA through Electrospinning [4]. PEI is a hyperbranched cationic polymer that can interact with polar groups on bacterial cell walls, leading to the destruction of bacterial cell membranes and achieving antibacterial effects. However, when the amount of PEI particles added exceeds 1% w/v, the mechanical properties of the material will decrease. Therefore, it is necessary to add SF to the PMMA-PEI system to increase the mechanical performance of the material. The text results indicate that the obtained material has both intrinsic antibacterial properties and higher elastic modulus and tensile stress compared to PMMA resin.

Zhang et al. synthesized functionalized birch resin derivatives (M1Bet and M2Bet) of monomethylacrylate and dimethylacrylate, and mixed them with bisphenol A glycerol dimethacrylate (Bis-GMA) and tri (ethylene glycol) dimethacrylate (TEGDMA) [5]. The results of this experiment demonstrate that when 10 wt% of M1Bet and M2Bet were added to Bis-GMA, the resin produced had good flowability and cell viability, while the polymerization rate was also relatively improved, and it can have good antibacterial activity against Proteus without sacrificing mechanical properties.

Cao et al. successfully synthesized a photo-curable polycation functionalized nanodiamond (QND) and used it as a nano filler to polymerize with a mixed resin (A blend of Bis-GMA and TEGDMA (50:50, weight ratio)) to form a new dental resin [6]. The repulsive force between the nanoparticles increases their compatibility with the resin matrix, so QND can be uniformly dispersed in the reinforced resin and improve the mechanical properties of the resin material. In addition, the resin added with QND exhibits anti-adhesion properties due to its hydrophilic surface, effectively reducing bacterial adhesion and achieving antibacterial effects.

Zhu et al. added Benzothiazole containing mono-methacrylate monomer (BTTMA) to the Bis-GMA/TEGDMA dental resin system, giving the system antibacterial properties [7]. The results showed that when the BTTMA content reached 20 wt.%, the resin material had significant antibacterial effects, and the antibacterial activity of the dental adhesive containing BTTMA was primarily from the immobilized BTTMA. Moreover, compared to the control resin material, the resin material containing BTTMA has lower polymerization shrinkage and water absorption.

3. Stimuli-responsive materials

The oral environment cannot remain unchanged, as daily eating, drinking, rest, and even mood changes can change the environment in the mouth. Therefore, resin based dental materials are exposed to different environments in the oral cavity, which requires dental materials to have the ability to adapt to different environments. Otherwise, it can lead to shorter material usage cycles, poorer treatment effects, and even secondary damage to teeth. For example, acid producing bacteria in the oral cavity can cause changes in pH, and the acid produced through metabolism can lead to a lower pH value on the surface of teeth, thereby damaging teeth and their repair materials. In order to cope with the impact of environmental changes in the oral cavity on resin based dental materials, in recent years, people have modified the materials, studied and prepared stimuli-responsive dental materials, so that resin based dental materials can respond to changes in the oral environment, increase the service life of the materials, and prevent secondary damage to teeth.

Stimuli-responsive materials, also known as smart materials, have the characteristic of responding to external stimuli. These stimuli can be changes in humidity, temperature, mechanical stress, or pH value. The photopolymerization reaction of dental composite materials is a stimulus reaction. pH is the most common stimulus utilized by scientists, and many materials targeting pH changes have been studied.

The specific surface area of nano amorphous calcium phosphate (NACP) is 35 times that of amorphous calcium phosphate (ACP). When it is added to PEHB resin with 5% 2-methacryloyloxyethyl phosphate choline (MPC) and 5% dimethylaminohexadecyl methacrylate (DMAHDM), a new dental material will be formed. This material can release calcium ions and phosphate ions when the pH value is too low. The released calcium ions and phosphate ions can form hydroxyapatite, which is conducive to the remineralization of Dentin and Tooth enamel. In addition, NACP is highly capable of neutralizing acids and increasing pH, as well as a certain ability to inhibit bacteria [8].

Liang et al. used tertiary amine (TA) as a modification material to endow resin based dental materials with antibacterial properties [9]. Two new TAs (dodecyl methylaminoethyl methacrylate (DMAEM) and hexadecyl methylaminoethyl methacrylate (HMAEM)) were introduced to the resin through the reaction of the acrylate group and methacrylate group. Because TA is an organic base and has a strong electron donating property at low pH, it is easy to form quaternary ammonium cation (QAM). Contact of negatively charged bacteria with the positively charged QAM site will kill the bacteria by disrupting their cell membrane's electrical balance [10]. New TA modified resin adhesives (TA@RAs) It has good long-term antibacterial stability, and when the pH is below the critical value, TA@RAs can quickly prevent the formation of biofilm, abate tooth demineralization, and subsequently avoid secondary caries. And the effect of TA@RAs on the normal microbiota is minimal after the pH value returns to normal, thus maintaining the oral environment.

Glass ionomer cements (GICs) are dental cements that harden through acid-base reactions using fluoroaluminosilicate glass as the main body. GIC has a gel structure, so its behavior is similar to that of human dentin when responding to temperature, pH or pressure, and other stimuli. When the oral pH of GIC drops to the critical pH value of 5.5, the fluoride it contains will be released, which can help teeth remineralize and inhibit demineralization behavior. However, traditional GIC has some drawbacks, such as long curing time, high hardness, and difficulty in polishing. Therefore, researchers have modified GIC with resin. The flexural strength of GIC was improved by adding Casein phosphopeptide (CPP) - amorphous calcium phosphate (ACP). The results showed that GIC containing 3% or 5% CPP-ACP could significantly inhibit the demineralization of Tooth enamel [11].

Lowson et al. prepared a kind of resin modified glass ionomer cements (RMGICs), which were composed of polyelectrolyte solution, hydroxyethyl acrylate (HEMA)/water mixture, and a small amount of photoinitiator for polymerization of HEMA [12]. When this RMGIC is exposed to ultraviolet radiation, it quickly hardens. At the same time, it also has strong adhesion, making it difficult for the material to detach after adhering to the teeth.

4. Self-repairing materials

In the complex oral environment, resin based dental materials will inevitably be affected by the external environment, such as bacterial erosion, changes in the acidity and alkalinity of the oral cavity, thermal expansion effects caused by temperature changes, or tooth collision and friction during chewing, which will cause some damage to the resin materials and lead to microcracks. Microcracks will gradually grow and fuse, ultimately leading to the rupture of resin materials and affecting their service life. In order to effectively overcome the micro-cracks generated by resin materials in various environments and extend the service life of the materials. Firstly, resin based dental materials can be antibacterial modified to reduce the impact of bacteria and their pH changes on the material; The second is to use materials that have similar responses to stimuli as human teeth, such as GIC. Third, self-healing microcapsule materials can also be introduced to resin based dental materials, endowing resin materials with self-healing properties [13].

Self-repairing microcapsule materials are typically composed of an internal core material and an external shell material, forming a typical core-shell structure. When microcracks occur, the microcapsules around the cracks are destroyed, and the healing solution inside of them reacts with the catalyst incorporated into the material., causing the resin to polymerize and achieve self-healing.

George et al. designed and developed a new type of self-healing dental composite material (SHDC) [14]. Compared to traditional dental composite materials, SHDC has two additional components: a healing powder (HP, fluoroaluminosilicate strontium particles) and a healing liquid (HL, polyacrylic acid aqueous solution encapsulated in silicon dioxide microcapsules). When microcracks damage the microcapsules, HL will be released from the microcapsules and react with HP to form reparative GIC within the cracks. The success of crack healing is proved by the Fracture toughness recovery experiment of SHDC, and the average healing efficiency can reach 25%.

Wu et al. prepared a dental composite with self-healing properties containing a polyurea formaldehyde (PUF) shell with TEGDMA and N, N-dihydroxyethyl p-toluidine (DHEPT) as the healing fluid [15]. The experimental results show that the addition of PUF microcapsules did not affect the original mechanical properties of the resin composite material, and the self-healing effect was directly proportional to the content of microcapsules in the composite material. When 7.5% microcapsules were added to the resin composite material, the self-healing effect can reach 64%~77%. At the same time, after 6 months of water aging, there was no significant change in the self-healing ability of the composite material with microcapsules added. Moreover, the self-healing effect of soaking in water was not significantly different from that of self-healing in air.

Chen et al. synthesized a resin composite with Dwifungsi for solving fracture and secondary caries [16]. It is composed of Bis-GMA-TEGDMA (mass ratio 1:1), 0.2 wt% camphorquinone (CQ) photo-initiator, 0.8 wt% ethyl-4dimethylobenzoate (EDMAB), and glass fillers silanized barium boroaluminosilicate. At the same time, a protein repellent composed of MPC was synthesized, which can reduce bacterial adhesion on the material surface. The experiment proved that the addition of 7.5 wt% MPC powder and 10 wt% TEGDMA-DHEPT microcapsule had no effect on the Flexural strength and elastic modulus of the composite. At the same time, the Fracture toughness (KIC) of the composite containing 10 wt% microcapsules was 36% higher than that of the control group. In addition, the addition of MPC did not damage the KIC of the composite. The healing ability of this resin composite material can reach 57% - 71%.

5. Conclusion

This paper mainly introduces some antibacterial materials, stimuli-responsive materials, and self-healing materials in resin based dental composites. It is precisely in order for patients to use better dental materials during treatment and reduce material aging caused by other factors that researchers continuously explore various new materials to achieve ideal results. Resin based dental composites have changed many fields of dental materials due to their beautiful and durable appearance, excellent mechanical properties, and ease of modification. However, they still have certain shortcomings, such as changes in the mechanical properties of the original resin composite material after modification. For antibacterial materials, organic synthetic antibacterial agents are highly toxic, easy to migrate, and have poor heat resistance; Natural antibacterial agents are limited by technological level and have limited application fields; Inorganic antibacterial agents are also toxic and have harsh usage conditions. For stimuli-responsive materials, the current dental materials can respond to a single stimulus but cannot achieve accurate multi-responses. For self-healing materials, their biggest shortcomings are their low self-healing rate and short duration. Therefore, resin based dental composites still have great prospects in the future, whether in material modification or clinical use.

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