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Fabrication of hybrid crosslinked network with buffering capabilities and autonomous strengthening characteristics for dental adhesives

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ABSTRACT

Ingress of bacteria and fluids at the interfacial gaps between the restorative composite biomaterial and the tooth structure contribute to recurrent decay and failure of the composite restoration. The inability of the material to increase the pH at the composite/tooth interface facilitates the outgrowth of bacteria. Neutralizing the microenvironment at the tooth/composite interface offers promise for reducing the damage provoked by cariogenic and aciduric bacteria. We address this problem by designing a dental adhesive composed of hybrid network to provide buffering and autonomous strengthening simultaneously. Two amino functional silanes, 2-hydroxy-3-morpholinopropyl (3-(triethoxysilyl)propyl) carbamate and 2-hydroxy-3-morpholinopropyl (3-(trimethoxysilyl)propyl) carbamate were synthesized and used as co-monomers. Combining free radical initiated polymerization (polymethacrylate-based network) and photoacid-induced sol-gel reaction (polysiloxane) results in the hybrid network formation. Resulting formulations were characterized with regard to real-time photo-polymerization, water sorption, leached species, neutralization, and mechanical properties. Results from real-time FTIR spectroscopic studies indicated that ethoxy was less reactive than methoxy substituent. The neutralization results demonstrated that the methoxy-containing adhesives have acute and delayed buffering capabilities. The mechanical properties of synthetic copolymers tested in dry conditions were improved via condensation reaction of the hydrolyzed organosilanes. The leaching from methoxy containing copolymers was significantly reduced. The sol-gel reaction provided a chronic and persistent reaction in wet condition-performance that offers potential for reducing secondary decay and increasing the functional lifetime of dental adhesives.

Statement of Significance

The interfacial gaps between the restorative composite biomaterial and the tooth structure contributes to recurrent decay and failure of the composite restoration. The inability of the material to increase the pH at the composite/tooth interface facilitates the outgrowth of more cariogenic and aciduric bacteria.

This paper reports a novel, synthetic resin that provides buffering capability and autonomous strengthening characteristics. In this work, two amino functional silanes were synthesized and the effect of alkoxy substitutions on the photoacid-induced sol-gel reaction was investigated. We evaluated the neutralization capability (monitoring the pH of lactic acid solution) and the autonomous strengthening property (monitoring the mechanical properties of the hybrid copolymers under wet conditions and quantitatively analyzing the leachable species by HPLC). The novel resin investigated in this study offers the potential benefits of reducing the risk of recurrent decay and prolonging the functional lifetime of dental adhesives.

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1. Introduction

Resin-based dental composite is the most widely used material for direct restorative dentistry [1–3]. In spite of this popularity, posterior composite restorations do not characteristically provide the durability associated with dental amalgam [4,5]. The primary reason that amalgam and composite restorations fail is recurrent decay, i.e. decay on the margins of existing restorations, but recurrent decay is 3.5 times greater for composite [6–12].

A clear difference between amalgam and composite is corrosion—the corrosion products seal defects at the tooth/amalgam interface but composite materials do not corrode. The adhesive that is used to bond the composite to the tooth is intended to seal discrepancies at the composite/tooth interface, but methacrylate-based dental adhesives/composites are vulnerable to hydrolytic and enzymatic degradation [4,13–16]. This degradation leads to gaps at the interface between the composite and tooth [17,18].

Another determining factor related to the failure of composite restorations is associated with bacterial adhesion and growth at the restorative material/tooth interface. *Streptococcus mutans* (*S. mutans*) is a gram-positive, facultative anaerobic microorganism that has been implicated as the major causative agent of dental caries [19–21]. Adhesion of *S. mutans* to the material/tooth interface creates an environment that supports the subsequent attachment and growth of other bacterial species, ultimately this activity leads to a micro-ecosystem known as a biofilm. In addition to its role as a “pioneer” organism in biofilm formation, *S. mutans* produces lactic acid; the lactic acid damages the adjacent tooth surface by demineralization [22]. With the degradation of dental adhesive and the formation of biofilm on the surface of restorative materials, enzymes, oral fluids and bacteria permeate the interfacial defects, undermining the composite restoration and bacteria destroy the adjacent tooth structure [23,24].

Various strategies have been developed to prevent or slow down the degradation of dental adhesives/composites [25–27]. However, due to the inherent water-absorption of methacrylate-based synthetic biomaterials, the degradation process in the oral environment is unavoidable and irreversible [4,13,28,29]. At the same time, the inability of the material to increase the pH at the composite/tooth interface facilitates the outgrowth of more cariogenic and aciduric bacteria [30–32]. Research has shown that successful restorative treatment does not alter the numbers of *S. mutans* [20,33]. Therefore, more effective methods for reducing the cariogenic challenge at the tooth/composite interface are needed. Materials that could neutralize the micro-environment at the tooth/composite interface offer the potential of protecting tooth structure and reducing the negative impact of bacteria at the margins of composite restorations [30]. With the emphasis on less invasive operative techniques, there is a pressing need to develop functionalized dental adhesives/composites capable of neutralization [34–36], bioactivity [37–39], or mineralization [40–42].

In our previous work, 2-N-morpholinoethyl methacrylate (MEMA) as amine-containing monomer ($pK_a = 6.2$) has been used to develop dental adhesive with neutralization capability [34]. MEMA-containing resin formulations showed good storage stability and MEMA-based copolymers showed low toxicity when used as a controlled drug-delivery system [43–45]. However, MEMA-functionalized copolymers showed fast neutralization behavior when loosely crosslinked network was formed, which would potentially limit the long-term performance of these materials under clinical conditions. Recently, we have developed a self-strengthening dental adhesive by introducing photoacid-induced

sol-gel reaction together with the free radical photopolymerization of methacrylate [46,47]. The results indicated that whether in wet conditions ($pH \sim 5.5$ @25 °C) or in acidic conditions ($pH \leq 3.5$ @25 °C), the sol-gel reaction is a suitable and novel approach to enhance the mechanical properties of the newly developed dental adhesive copolymers [46,47].

In this study, two amino functional alkoxy silanes were synthesized and incorporated in a dental adhesive formulation to provide a hybrid material with neutralization capabilities and self-strengthening characteristics. We first evaluated the effect of different alkoxy groups of silane on the hydrolysis/condensation of the sol-gel reaction. We next investigated the neutralization behavior and mechanical properties of the hybrid copolymers following prolonged aqueous storage. The present study tests the hypothesis that: i) the amine group built-in to the dental adhesive network by photoacid-induced sol-gel reaction can neutralize lactic acid, and ii) the mechanical properties of dental adhesive can be improved in wet conditions. By combining neutralization capacity and self-strengthening characteristics, the developed hybrid copolymers are postulated to serve as dental adhesives that provide better long-term performance in the oral environment.

2. Materials & methods

2.1. Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (BisGMA), 2-hydroxyethyl methacrylate (HEMA), camphorquinone (CQ), ethyl-4-(dimethylamino) benzoate (EDMAB), diphenyliodonium hexafluorophosphate (DPIHP), L(+)-lactic acid (LA), dibutyltin dilaurate (DBTL), 3-morpholino-1,2-propanediolb (MPD), and (3-isocyanatopropyl) triethoxysilane (IPTES), were obtained from Sigma-Aldrich (St. Louis, MO) and used as received without further purification. (3-isocyanatopropyl) trimethoxysilane (IPTMS, 95%) was purchased from Gelest Inc., (Morrisville, PA). 2-hydroxy-3-morpholinopropyl (3-(triethoxysilyl)propyl) carbamate (SNE), 2-hydroxy-3-morpholinopropyl (3-(trimethoxysilyl)propyl) carbamate (SNM) were synthesized in our laboratory and used as co-monomers (see SI Scheme 1). All other chemicals were used as received without further purification.

2.2. Synthesis of co-monomer SNE/SNM

The new co-monomers, SNE/SNM, were synthesized based on the following procedures [48]. Briefly, to a 250-mL, round bottom flask, fitted with a magnetic stirrer and N_2 -purging, MPD (4.20 g, 25 mmol), DBTL (20 μ L) and tetrahydrofuran (THF, 50 mL) were added. When the temperature was cooled to 0 °C with an ice-water bath, IPTES (6.38 g, 25 mmol, for SNE) or IPTMS (5.13 g, 25 mmol, for SNM) dissolved in 40 mL THF was added stepwise over a 2 h period. Next, the reaction mixture was kept at 0 °C for 4 h and raised to 23 ± 2 °C for another 20 h. The progress of the reaction was followed by FTIR (Spectrum 400 Fourier transform infrared spectrophotometer, Perkin-Elmer, Waltham, MA) to monitor the disappearance of isocyanate (NCO) at 2266 cm^{-1} . After the reaction was completed, THF was removed by rotary evaporation and ethyl acetate (100 mL) was added to dissolve residual liquid. Then 100 mL saturated NaCl solution was added to wash the unreacted starting materials. The EA oil-phase was dried over anhydrous $MgSO_4$ and followed by removing the solvent with a rotary evaporator at 40 °C to obtain as colorless oil SNE (7.65 g, 75% theory). THF was removed from SNM after the reaction was completed by rotary evaporation to obtain viscous colorless oil (8.06 g, 88% theory).

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