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Acidic pH weakens the bonding effectiveness of silane contained in universal adhesives

*Chenmin Yao, Jian Yu, Yake Wang, Chuliang Tang, Cui Huang**

The State Key Laboratory Breeding Base of Basic Science of Stomatology (Hubei-MOST) & Key Laboratory for Oral Biomedicine Ministry of Education, School & Hospital of Stomatology, Wuhan University, Wuhan, China

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ABSTRACT

Objectives. Some silane-containing universal adhesives were introduced that a separate ceramic primer was unnecessary to glass-ceramic bonding because of incorporated silane. We aimed to investigate the effectiveness of silane in universal adhesives with acidic media.

Methods. A functional γ-methacryloxypropyltrimethoxysilane (γ-MPTS) was used, and its pH value was adjusted to 2.7 by adding hydrochloric acid (HCl) or 10-methacryloxydecyl phosphate (MDP). The prepared acidic silane solutions after 2 h or 10 d storage were characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Micro-shear bond strength (μSBS) was used to evaluate the bonding performance of glass ceramics. Two silane-containing and two silane-free universal adhesives were included. Field-emission scanning electron microscopy fractography analysis was also performed.

Results. FTIR, ^{1}H and ^{13}C NMR revealed that the hydrolysis of γ-MPTS and the self-condensation reaction of silanol groups occurred over time under acidic conditions (HCl or MDP solution). This reaction formed the siloxane oligomers. For glass-ceramic bonding, the μSBS of acidic silane after 10 d storage was lower than that of silane stored for 2 h storage ($p < 0.05$), although the difference among the μSBS of the four universal adhesives were nonsignificant ($p > 0.05$). Additionally, cohesive failure was the main fracture pattern of universal adhesive bonding.

Significance. The effectiveness of silane contained in low pH universal adhesives can be weakened by dehydration self-condensation and consequently became unstable. For the enhancement of glass-ceramic bonding efficiency with universal adhesives, a separate ceramic primer was recommended.

1. Introduction

Silane coupling agents are widely used in restorative dentistry, mediating the adhesion between inorganic and organic materials [1]. γ-Methacryloxypropyltrimethoxysilane (γ-MPTS) is one of the most common functional silane monomer used for dental applications [2,3]. Especially for silica-based ceramic bonding, the application of a silane coupling agent is rec-

* *Corresponding author at*: School & Hospital of Stomatology, Luoyu Road #237, Hongshan District, Wuhan 430079, China.
E-mail address: huangcui@whu.edu.cn (C. Huang).

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ommended because bifunctional silane molecules can form a siloxane network with ceramic surfaces and copolymerize with composite resin [4,5]. Besides, silane has the property in facilitating the adhesion among fiber posts [6,7], silica-coated titanium [8], and intra-oral repairs of ceramic and composite resin [9]. However, the application of commercial silane remains limited because of its short shelf life and bond degradation [10,11]. Therefore, the chemical effectiveness and stability of silane should be improved for long-term clinical bonding performance and in-depth investigations.

Generally, the silane monomer can be activated and hydrolyzed in an aqueous acetic acid solution. In particular, functional silane monomers need to be activated for the formation of silanol groups before bonding. Then, the chemical bonding of oxane (Si—O—Si) between silane and hydroxyl groups on a substrate surface occurs [12]. However, high molecular weight siloxane oligomers, which were formed through the dehydration self-condensation of silanol, may affect the initial activities of silane monomers [13,14]. Moreover, the hydrolysis and self-condensation of silane are affected by the pH value of a solution [15], solvent system, and temperature [10]. Generally, common silane used in dentistry has a pH value between 4 and 5 [16]. A previous study suggested that, with respect to organotrialkoxysilanes, silane is highly stable when the pH value of the solution is approximately 4. This phenomenon can be illustrated by the minimum rate of condensation between the silanol groups, which trend to form large oligomers [1]. Recently, some silane-containing "universal adhesive" with a low pH value were introduced, such as the Single Bond Universal (SBU; 3M ESPE, St. Paul, MN, USA, pH 2.7) and Clearfil Universal Bond (CUB; Kuraray Noritake Dental, Tokyo, Japan, pH 2.3). Thus, in the above acid environment, the effectiveness and long-term stability of silane contained in the universal adhesive is a critical concern to both dentists and researchers.

Apart from silane, some universal adhesives also contain 10-methacryloxydecyl phosphate (MDP) as an acidic functional monomer. MDP is mainly used for enhancing the effectiveness of dentin bonding and zirconia bonding [17,18]. In tooth tissues, MDP can have a chemical interaction with hydroxyapatite and form stable MDP-Ca salts [19,20]. MDP can also react with zirconia and generate the P—O—Zr covalent bond by the organophosphate ester group [21]. Nevertheless, previous studies found that the pH value of commonly used MDP is between 2 and 2.7 [17,22]. As mentioned above, the stability of functional silane may be affected by a low pH value. Although silane and MDP are both important functional monomers in dentistry and widely used, limited information is available on the silica-based ceramic bonding involving silane and MDP in a universal adhesive. Furthermore, the effectiveness of silane incorporated with a low pH MDP-containing universal adhesive is rarely studied.

Therefore, we attempted to determine whether the low pH values of universal adhesives affect the effectiveness of incorporated silane. Acidic MDP was also added in the experimental silane solution. We subsequently performed Fourier transform infrared spectroscopy (FTIR) [13,23,24] and nuclear magnetic resonance (NMR) [12,14,25] to reveal the hydrolysis and self-condensation information of silane. The chemical characteristics of silane were analyzed through FTIR, ^{1}H NMR, and ^{13}C NMR. Furthermore, micro-shear bond strength measurements were performed for the analysis of the mechanical properties of silane and universal adhesives. We hypothesized that (1) the effectiveness of silane in universal adhesives will not be impaired in acidic environment induced by acidic MDP, and (2) silane will maintain its stability in such acidic environment with time.

2. Materials and methods

2.1. *Preparation of silane solution*

The specifications for the preparation of different silane solutions are illustrated in Fig. 1. A silane solution was prepared consisting of 10% γ-MPTS (Aladdin, Shanghai, China) and ethanol by volume. Another solution was mixed with 10% γ-MPTS, ethanol and acidic 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP; DM Healthcare Products, Inc., San Diego, CA, USA). The main materials used in the study are shown in Table 1. The pH values of the experimental silane solutions were adjusted to 2.7 with a pH meter (Mettler Toledo, FE20-FiveEasy, Zurich, Switzerland). Before the analysis, the prepared samples of the silane solution were kept in storage for either 2 h or 10 d.

2.2. *Fourier transform infrared spectroscopy (FTIR) analysis*

Each silane solution (solution 1: pure silane after 2 h storage; solution 2: 10% silane with HCl after 2 h storage; solution 3: 10% silane with MDP after 2 h storage; solution 4: pure silane after 10 d storage; solution 5: 10% silane with HCl after 10 d storage; and solution 6: 10% silane with MDP after 10 d storage) was placed on a KBr plate. The solvent was evaporated under an infrared lamp for approximately 10 s. Then, FTIR analysis was conducted. An FTIR spectrophotometer (Nicolet 5700, Thermo Electron Scientific Instruments Corp, MA, USA) was used at room temperature. All transmission spectra were obtained at a resolution of 4 cm^{-1} with range of 400–4000 cm^{-1}. The infrared spectrum of each experimental solution was recorded three times.

2.3. *NMR analysis of different silane solutions*

The hydrolysis and condensation reaction of the different silane solutions (i.e., 10% silane, 10% silane with HCl or MDP after 2 h storage; 10% silane, 10% silane with HCl or MDP after 10 d storage) were analyzed with an NMR spectrometer (Bruker AVANCE III HD, Switzerland) in a deuterated methanol (CD_3OD). The ^{1}H and ^{13}C NMR spectra of the silane solutions were operated at 400 MHz and 100.58 MHz, respectively. The best resolution for proton and carbon was obtained by calibrating the spectral widths and by measuring chemical shifts with tetramethylsilane (TMS) solution as reference. The ^{1}H NMR spectra were referenced at the internal CD_3 peak ($\delta = 3.31$ ppm) of CD_3OD, while ^{13}C NMR spectra were referenced at the peak ($\delta = 49.00$ ppm).

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