DENTAL MATERIALS XXX (2017) XXX–XXX

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Zirconia surface modification by a novel zirconia bonding system and its adhesion mechanism

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ARTICLE INFO

Article history:
Received 10 May 2017
Received in revised form
8 August 2017
Accepted 7 September 2017
Available online xxx

Keywords:
Zirconia
H_2O_2 oxidation
Zirconium alkoxide
Silane
Bond strength
XPS

ABSTRACT

Objective. Bonding to zirconia has been of great interest over the last 10–15 years. The aim of this study was to develop a zirconia bonding system and clarify its adhesion mechanism.
Methods. A zirconia primer was prepared using tetra-*n*-propoxy zirconium (TPZr) and water. A silane primer was also prepared using γ-methacryloyloxypropyltrimethoxysilane (γ-MPS) and hydrochloric acid. After the zirconia primer was applied to the oxidized zirconia surface, the silane primer was applied to the ZrO_2-functionalized layer and the resin cement was applied to the silane-modified layer. Ceramic Primer II was used as a typical MDP-based ceramic primer. Shear bond strengths were measured using a universal testing machine. To clarify the enhancing mechanism of the zirconia bonding system, X-ray photoelectron spectroscopy (XPS) analyses were performed.
Results. The zirconia bond strength was affected by the surface wettability of zirconia, and the compositions of TPZr and water utilized in the zirconia primer. When the zirconia primer, consisting of 10 μL TPZr and 13 μL water, was applied to the zirconia surface that had been oxidized by H_2O_2 above 10%, the maximum bond strength of 8.2 MPa was obtained. The mechanism of the zirconia bonding system was established as follows: the hydrolyzed zirconium species formed a more reactive ZrO_2-functionalized layer on the oxidized zirconia surface, and the hydrolyzed γ-MPS species adsorbed on that layer introduces a chemical bonding to the resin.
Significance. The novel zirconia bonding system enhanced the bonding performance of the resin, and showed a greater bond strength than an MDP-based ceramic primer.

1. Introduction

Increasing demands for esthetics [1–3], biocompatibility [4–6] and reduced risks of metal allergies [7,8] have led to the development of ceramics with high mechanical strength and high translucency, such as yttria- and ceria-stabilized

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http://dx.doi.org/10.1016/j.dental.2017.09.001

Table 1 – Materials and chemicals used in this study and their abbreviations, manufacturers, lot numbers, and countries.

Materials	Abbreviation	Manufacturer	Lot number	City, country
Aadva Zirconia NT	Zirconia	GC CO.	1411031	Tokyo, Japan
LinkMax	–	GC CO.	1608091	Tokyo, Japan
Ceramic Primer II	CP	GC CO.	1510162	Tokyo, Japan
Chemicals	Abbreviation	Manufacture	Lot number	City, Country
Tetra-*n*-propoxy zirconium	TPZr	Matsumoto Fine Chemical	B6161	Chiba, Japan
γ-Methacryloyloxypropyltrimethoxysilane	γ-MPS	Shin-Etsu Chemical CO., Ltd.	810345	Tokyo, Japan
Hydrogen peroxide	H_2O_2	Wako Pure Chemical Inds	DSK6811	Osaka, Japan
2-Propanol	–	Wako Pure Chemical Inds	ECG4349	Osaka, Japan
0.1 mol/L hydrochloric acid solution	–	Wako Pure Chemical Inds	PDJ0047	Osaka, Japan
Ethanol	–	Wako Pure Chemical Inds	EBR2882	Osaka, Japan

tetragonal zirconia polycrystals. Those materials are used for dental applications, such as frameworks and full crowns, because their martensic transformation enhances their flexural strength and toughness to a level superior to all other ceramic materials [9–11]. Over the last 10–15 years, bonding to zirconia has become a topic of great interest [12–14]. This is due to traditional silane chemistry is, without any pre-treatment of the zirconoia surface, ineffective in bonding performance, since the surface characteristic of zirconia is chemically inert in contrast to silica-based ceramics [15].

To improve the zirconia bonding performance of resin cements by using a silane coupling agent, tribochemical silica coating technique have been introduced [16–23]. Martinlinna et al. reported that several types of silane coupling agents enhanced the bond strength to the zirconia surface silica-coated by tribochmical technique [16,18]. Furthermore, Piascik et al. [24] introduced a unique silica-coating technique for grit-blasted zirconia surfaces to promote chemical bonding with traditional silanes using a vapor-phase mixture of tetrachloro-silane and water. Recently, many research groups have focused on functional phosphate monomers, such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP) [25–27]. This is due to the fact that the phosphate group in MDP forms a chemically-stable covalent bond to a zirconia surface (—P—O—Zr) the same as that of an organophosphate, octyl phosphate [28]. However, that study recommended the combination of grit blasting with the MDP-based ceramic primer, since the ability of MDP to enhance the bond strength of the resin is very poor and all bonded specimens shows an interfacial failure of the resin from the zirconia surface [29]. However, we should remember that grit-blasting approaches may cause initial fracture that will lead to premature and catastrophic failure [30–33]. The development of a novel chemical bonding method is therefore in great demand.

In this study, we developed a convenient zirconia bonding system to introduce chemical bonding with a resin cement. This system consists of three steps: (1) H_2O_2 oxidation of the zirconia surface, (2) functionalization of the oxidized zirconia surface with a zirconia primer, and (3) silanization of the ZrO_2-functionalized surface with a traditional silane primer. The null hypothesis tested was that: (1) the concentration of H_2O_2 has no effect on the ability of the zirconia primer to enhance the zirconia bonding performance of the traditional silanization and bonding techniques, and (2) the amounts of tetra-*n*-propoxy zirconium (TPZr) and water that constitutes the two-bottle type zirconia primer have no effect on the bonding performance of the resin.

2. Materials and methods

2.1. Materials

The materials and chemicals used in this study are listed in Table 1.

2.2. Methods

2.2.1. Preparation of adherend

The surfaces of yttria-stabilized zirconia disks (ZrO_2 87 mass%, Y_2O_3 9 mass%, HfO_2 3 mass%, Al_2O_3 1 mass%; diameter: 12 mm, thickness: 5 mm) were ground using a sequence of 240-, 320-, 400-, 600-, 800-, 1000-, 1200-, 1500- and 2000-grit silicon carbide papers under a stream of water. Thereafter, those surfaces were polished using a sequence of 4000-, 6000-, 8000- and 10000-grit wrapping film sheets under water irrigation.

After being polished, each zirconia surface was oxidized by immersion of the zirconia disk in H_2O_2 at 60 °C for 6 h. The quantity of H_2O_2 solution was determined as 10 mL to oxidize each zirconia disk, $2 \times (6 \times 6 \times \pi) + (2 \times 6 \times \pi) \times 5\,mm^2$ in size. The concentration of H_2O_2 was fixed at 0, 3, 5, 10 and 20 mass%. The oxidized zirconia surfaces were used as adherend surfaces.

2.2.2. Measurement of contact angle of a water drop to oxidized zirconia surface

The surface wettability of the oxidized zirconia samples was characterized by measuring the contact angle of a water drop using a contact angle meter (DropMaster: DM100, Kyowa Interface Science, Niiza, Saitama, Japan). Measurements were made at two different locations on each sample at 3 s after application of the droplet. The volume of the water drop was maintained at 0.5 μL. The number of samples was 16 in each experimental group.

2.2.3. Preparation of the two-bottle type zirconia primer

A two-bottle type of experimental zirconia primer, which consists of a zirconium alkoxide solution and an activator solution, was prepared after dissolving TPZr and water in 2-propanol, respectively. The amounts of TPZr and water added in the respective solutions are summarized in Table 2.

2.2.4. Preparation of the two-bottle type silane primer

Based on our previous studies [34–37], we designed a two-bottle type silane primer, consisting of a silane solution and an activator solution were prepared using

Please cite this article in press as: Murakami T, et al. Zirconia surface modification by a novel zirconia bonding system and its adhesion mechanism. Dent Mater (2017), http://dx.doi.org/10.1016/j.dental.2017.09.001