dental materials 28 (2012) 863–872

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Resin zirconia bonding promotion with some novel coupling agents

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ARTICLE INFO

Article history:
Received 30 November 2011
Received in revised form
22 February 2012
Accepted 16 April 2012

Keywords:
Resin composite
Zirconia
Adhesion
Coupling agent
Bond strength

ABSTRACT

Objectives. To evaluate and compare three novel coupling agents: 2-hydroxyethyl methacrylate, itaconic acid and oleic acid to two silane coupling agents, one commercial silane product and 3-acryloxypropyltrimethoxysilane on the bond durability of resin composite to zirconia.

Methods. Zirconia samples were silica-coated by air abrasion and each of the five coupling agents was then applied to give five test groups. Resin composite stubs were bonded onto the conditioned zirconia surfaces. The samples were stored: dry storage, 30 days in water and thermocycled to give a total of fifteen test groups. The shear bond strengths were determined using a universal testing machine and data analyzed by two-way ANOVA and Tukey HSD ($p < 0.05$) with shear bond strength as dependent variable and storage condition and primers as independent variables. The bond formation of the five coupling agents to zirconia was examined by X-ray photoelectron spectroscopy (XPS).

Results. Two-way ANOVA analysis showed that there was a significant difference for different primers ($p < 0.05$) and different storage conditions ($p < 0.05$) on the shear bond strength values measured. XPS analysis showed a shift in binding energy for O_{1s} after priming with the five coupling agents which revealed different bond formations related to the functional groups of the coupling agents.

Significance. The shear bond strength values measured for all coupling agents after water storage and thermocycling exceed the minimum shear bond strength value of 5 MPa set by ISO. The silane coupling agent, 3-acryloxypropyltrimethoxysilane, showed the highest bond strength of the three storage conditions.

1. Introduction

Zirconia is used as a biomaterial because of superior mechanical properties, chemical inertness and biocompatibility [1]. Normally, zirconia is doped with a small amount of yttria (Y_2O_3) to form yttria tetragonal zirconia polycrystals (TZP) which increases the fracture toughness, flexural strength and wear resistance [2]. Yttria tetragonal zirconia polycrystals are widely used in dentistry as root canal posts, orthodontic brackets, dental implant abutments and all-ceramic restorations [3]. Inertness of zirconia has made resin to zirconia

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0109-5641/$ – see front matter
http://dx.doi.org/10.1016/j.dental.2012.04.023

bonding challenging. Tribochemical silica-coating using a Rocatec system followed by silanization has been suggested as a pre-treatment before cementation [4]. Other zirconia surface treatment methods have been reported, these include: chemical treatments, selective infiltration etching, laser irradiation, nano-structured alumina coating and chemical vapor deposition [5–11]. All of these treatment methods, with different surface conditioning mechanisms, activate the zirconia surfaces for bonding to resin composite.

A coupling agent has two different functional groups so as to connect dissimilar materials, such as metals to polymers. Silane coupling agents are widely used to promote adhesion of dental restorations to tooth tissue [6]. Due to the large variety of silane coupling agents with different functional groups, numerous *in vitro* studies of experimental silane coupling agents in resin zirconia bonding have been investigated [12–15]. 3-Acryloxypropyltrimethoxysilane (Fig. 1) is a promising coupling agent with *in vitro* results comparable to other silane coupling agents under dry and artificial aging conditions [13,15]. Coupling agents such as phosphates, *e.g.* 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and zirconates have also been investigated for resin to zirconia bonding [16,17] with the former gaining popularity as an alternative to silane coupling agents because of enhanced bonding and hydrolytic stability [18]. However, some studies report that the bond durability under artificial aging of resin to zirconia primed with silane coupling agents is higher than that primed with phosphate coupling agents [19,20].

The three novel coupling agents for resin zirconia bonding investigated in this study were: 2-hydroxylethyl methacrylate, itaconic acid and oleic acid. 2-Hydroxylethyl methacrylate, contains a >C=C< and —OH group and itaconic acid and oleic acid, contain >C=C< and —COOH groups (Fig. 1). These coupling agents have many applications in industry and medicine [21–28]. 2-Hydroxylethyl methacrylate has been used for the surface modification of a polysulfone membrane for treatment of oily wastewater, contact lens applications and synthesis of macroporous hydrogels for adsorption of proteins for biomedical applications. Itaconic acid is added to vinylidene chloride coatings to improve adhesion to paper and cellophane. The reaction of itaconic acid with amines forms N-substituted pyrrolidones which can be used as thickeners in lubricating grease, shampoos, detergents, pharmaceuticals and herbicides. In medicine, esters of partly substituted itaconic acid have anti-inflammatory and analgesic properties. Oleic acid, *n*-octadecan-9-enoic acid, is a mono-unsaturated omega-9 fatty acid which can be found in olive oil. It has been used as a drug delivery vehicle for the medical management of keloid and hypertrophic scaring. It is also used as a protective coating on mild steel against corrosion, solvent attack and as an environmentally friendly biolubricant. In addition, 2-hydroxylethyl methacrylate has been used successfully in resin dentin bonding [29–31]. Other coupling agents with the functional group (—COOH) are also found in dentin adhesives, these include 4-methacryloxyethyl trimellitic acid and 11-methyacryloyloxy-1,1′-undecanedicarboxylic acid [32,33].

The aim of this *in vitro* study was to evaluate and compare the bond durability of the three novel coupling agents, 2-hydroxylethyl methacrylate, itaconic acid and oleic acid, to two silane coupling agents, one commercial dental silane product and one experimental silane coupling agent, 3-acryloxypropyltrimethoxysilane, for resin composite to zirconia bonding under different storage conditions. The hypothesis was that there is no difference in bond durability between the three novel coupling agents and the two silane coupling agents under different storage conditions.

2. Materials and methods

Zirconia blocks (Lava, 3 M ESPE, Seefeld, Germany) were cut into blocks of 16 mm × 15 mm × 3 mm and embedded in cylindrical plastic molds filled with poly(methylmethacrylate) resin. Five test groups of resin composite were bonded to silica-coated and primed zirconia and investigated under three different storage conditions, giving a total of fifteen experimental groups of randomly assigned samples. Each experimental group consisted of 15 resin composite stubs for bond strength measurement. The 3 M ESPE Sil silane is a pre-hydrolyzed dental silane product of 3-methacryloxypropyltrimethoxysilane (Fig. 1), at a silane content of "<3 vol.%", indicated for silica-coated metallic and ceramic indirect restorations [4,6].

2.1. Preparation of silica-coated zirconia samples

The zirconia sample surfaces were polished with a 400-grit silicon carbide paper under running deionized water, then cleaned ultrasonically for 10 min in deionized water and rinsed with deionized water. They were allowed to dry in air at room temperature for 30 min. Silica-coating of the polished zirconia specimens was performed using Rocatec Sand Plus (110 μm in size of silica-coated alumina particles, 3 M ESPE, Seefeld, Germany) at a constant pressure of 280 kPa for 30 s/cm^2 and at a perpendicular distance of 10 mm [34]. The samples were then cleansed in an ultra-sonic bath in 70% ethanol for 10 min and then rinsed with 70% ethanol. They were allowed to air-dry at room temperature for 30 min.

2.2. Preparation of primer solutions and primer coating on zirconia surface

A silane solution of 1.0 vol.% of 3-acryloxypropyltrimethoxysilane (95%, Gelest, Morrisville, PA, USA) in a solvent mixture of 95.0 vol.% absolute ethanol (99.8%, Riedel-de Haën, Seelze, Germany) and 5.0 vol.% deionized water was prepared. The pH of the solvent mixture was adjusted to 4.0 by 1 M acetic acid. The silane solution was then allowed to hydrolyze for 1 h [12].

Solutions of 1.0 vol.% 2-hydroxyethyl methacrylate (98%, Sigma, St. Louis, MO, USA), itaconic acid (BDH, PA, USA) and oleic acid (92%, BDH, PA, USA) were all prepared in a solvent mixture of 95.0 vol.% acetone (99.9%, VWR International SAS) and 5.0 vol.% deionized water. The pH of the solvent mixture was adjusted to 4.0 by 1 M acetic acid. These three coupling agents do not require hydrolysis. The five primer solutions were applied onto the silica-coated zirconia surfaces with one coating using a new fine brush each time. This was allowed to dry and react for 5 min, before the next bonding step.