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Short Communication

Effects of a zirconate coupling agent incorporated into an experimental resin composite on its compressive strength and bonding to zirconia

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ABSTRACT

Aim: To assess *in vitro* the compressive strength of an experimental zirconate coupling agented resin composite and its bonding to dental zirconia ceramics.
Methods: Various ratios (1.5–4.0 wt%) of a zirconate coupling agent, NZ-33®, zirconium(IV)-2,2[(bis-2-propenolatomethyl)butanolato-tris-2-methyl-2-propenoato-O)] were incorporated in an experimental *bis*-GMA/MMA-based resin composite formulation with silica fillers. Compressive strength of the experimental resin composite and shear bond strength (SBS) of the resin composite to zirconia were evaluated by using a universal testing machine. Specimens were stored in dry condition, in water storage for 7 days and for 14 days, to a total of twenty test groups. The data were analyzed by one-way ANOVA and Tukey post hoc test ($\alpha=0.05$).
Results: SBS of resin-to-zirconia bonding and compressive strength both have significant increase at 1.5 wt% and 3.0 wt% NZ-33® ($p<0.05$). However, water storage for 7 days ($p>0.05$) and 14 days ($p>0.05$) significantly decreased SBS of the experimental resin-to-zirconia with no significant difference between groups ($p>0.05$).
Conclusions: An addition of a zirconate coupling agent used might strengthen the biomechanical properties of the experimental resin composite.

1. Introduction

Zirconia may have the best mechanical properties among all the oxide ceramics available today (Warashina et al., 2003; Liu et al., 2012). However, there is still no unanimous clinical recommendation for cementation for zirconia. One widely used way to do it is first to modify the zirconia surface topology by sandblasting and cleanse it (Kern, 2009) and then silanize it with a silane coupling agent (Lung and Matinlinna, 2012) before cementation. Successful and durable adhesion depends on micromechanical retention and chemical bonding. Studies had shown that typical conventional cementation methods might not give satisfactory bond strengths to zirconia surfaces (Blatz et al., 2003; Kojima et al., 1997). Tribochemical silica-coating might be effective on zirconia surface as a silica layer is deposited and then formation

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of siloxane bonds with a silane primer after silanization (Matinlinna et al., 2006a, 2007, 2013; Lung and Matinlinna, 2010). Deposition of small amount of silica after tribochemical silica-coating was observed. This may be explained by the fact that zirconia is too hard to allow silica particles embedded in the dense and hard zirconia matrix (Thompson et al., 2011). Nevertheless, a better surface treatment and adhesion system might be necessary. Furthermore, the currently used two- or three-step priming procedures are somewhat cumbersome to dental practitioners.

Resin composites are polymeric-based materials that have been used as dental restorative materials and luting cements since 1960s (Garoushi et al., 2011). They consist of five main components: (1) inorganic filler, (2) coupling agent, (3) organic resin matrix, (4) pigments and (5) initiator–accelerator system. The coupling agent links the dissimilar inorganic filler and organic resin matrix together to form a bulk material (Lung and Matinlinna, 2012). In fact, some coupling agents such as 10-methacryloxydecyl dihydrogen phosphate (MDP) might have a strong chemical interaction tendency with zirconia surfaces (Kojima et al., 1997; Yoshida et al., 2006; Mayet al., 2010). Thus, it is possible to skip the application of primer on the zirconia surface before cementation. Some studies have reported that bond degradation of resin composite to zirconia with MDP primer takes place under thermal cycling. Most of the tested specimens showed adhesive failure at the zirconia–resin cement interface (Kern and Wegner, 1998; Wegner and Kern, 2000; Blatz et al., 2004).

It has been proposed to use other coupling agents, such as zirconate coupling agent, which may be an alternative to the conventional silane coupling agent or even the new ones like MDP (Yoshida et al., 2006). Zirconate coupling agents are usually used to increase toughness of thermoplastics in technology, and make finer and more uniform foamed polymers in modern industrial applications. Recently, only few studies (Yoshida et al., 2006), have been carried out on using zirconate coupling agents in dentistry. Zirconia is a biocompatible material of choice in dentistry (Mallineni et al., 2013). The aim of this pilot laboratory study was to assess the effect of a zirconate coupling agent on an experimental resin composite. The resulting compressive strength and its shear bond strength to zirconia bonding were investigated.

2. Materials and methods

2.1. *Preparation of the experimental resin composite*

The materials used in this study are listed in Table 1. Firstly, a fixed ratio of methyl methacrylate (MMA) (Accu-Chem Industries Inc., Melrose Park, IL, USA), camphorquinone (CQ) (Accu-Chem Industries Inc.) and *N, N*-cyanoethyl methylaniline (CEMA) (Accu-Chem Industries Inc.), were mixed together with addition of various ratios from 0 to 4 wt% of a zirconate coupling agent (NZ-33®, Kenrich Petrochemicals Inc., Bayonne, NJ, USA). The mixture was stirred in a plastic beaker. Next, 30 wt% of the final mass of the experimental resin matrix, silica fillers (AL-1FP, W.R.Grace & Co., USA) and respective ratios of *bis*-phenol α-glycidyl methacrylate (*bis*-GMA) were added to the mixture. The filler ratio of 30 wt% of total weight was chosen to produce a yellowish resinous paste which would not be too fluid or too viscous. Thus, the matrix part was composed of 70 wt% of the total mass of the resin composite. This paste was transferred to plastic syringes which were carefully wrapped in an aluminum foiland stored in a refrigerator. The mixed ratios of experimental resin composite are shown in Table 2.

2.2. *Surface treatment of zirconia by sandblasting*

The circular unsintered zirconia discs (Upcera, China) with a diameter of ca. 10 cm were cut into square blocks (~1 cm × 1 cm). A polishing machine (Lunn Major, Struers, Denmark) was used to polish all sides of the zirconia blocks. The cut zirconia pieces were cleansed with 70 wt% ethanol solution (BDH Reagents & Chemicals, UK) in an ultrasonic bath (Decon

Table 1 – Materials used in the study.

Product	Model No.	Purity	Manufacturer	City and country	Lot. No.
bis-GMA	B03844	AR	Accu-Chem Industries Inc.	Melrose Park, IL, USA	MKBJ3076V
MMA	M98047	AR	Accu-Chem Industries Inc.	Melrose Park, IL, USA	M98047
CQ	C15457	≥99.0%	Accu-Chem Industries Inc.	Melrose Park, IL, USA	51211
CEMA	C28543	≥98.5%	Accu-Chem Industries Inc.	Melrose Park, IL, USA	NXYAD
Silica Filler	AL-1FP	/	W.R.Grace & Co.	Columbia, MD, USA	1000163698
Zirconate coupling agent	NZ-33	/	Kenrich Petrochemicals Inc.	Bayonne, NJ, USA	28957
Zirconia	U98-10W52	/	Shenzhen Upcera Co., Ltd	Shenzhen, Guangdong, China	S2110815198

Table 2 – Matrix composition (in wt%) for the experimental groups.

	bis-GMA	MMA	CQ	CEMA	NZ-33
0.0% (Control)	78.0	20.0	1.0	1.0	0.0
1.5%	76.5	20.0	1.0	1.0	1.5
2.5%	75.5	20.0	1.0	1.0	2.5
3.0%	75.0	20.0	1.0	1.0	3.0
3.5%	74.5	20.0	1.0	1.0	3.5
4.0%	74.0	20.0	1.0	1.0	4.0