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Effects of silica-coating and a zirconate coupling agent on shear bond strength of flowable resin–zirconia bonding

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ABSTRACT

The aim of this *in vitro* study was to evaluate the effect of tribochemical silica-coating and a zirconate coupling agent application on bonding between a resin composite and zirconia. Firstly, it was hypothesized that the zirconate coupling agent modified surface would promote higher and more stable shear bond strength than a surface treated with tribochemical coating only. Secondly, the modified surface would retain its bond strength after artificial aging. The shear bond strength between a resin composite bonded to surface treated zirconia was measured. Hydrolytic stability of this bond was verified after water storage while the interface chemistry was evaluated using energy dispersive x-ray analysis. Surface treatment showed significantly greater shear bond strength compared with no treatment before artificial aging while specific surface treatments showed higher shear bond strength compared with no treatment after artificial aging. The predominant mode of failure after shear bond testing was adhesive. Energy dispersive x-ray analysis at the surface revealed elemental C_{1s}, O_{1s}, Si_{1s} and Zr_{2p}. As a result, tribochemical silica-coating followed by application of a zirconate coupling agent was suggested to create a successful a resin-to-zirconia bonding. Further investigation is required as reference for clinical approach in the cementation of zirconia restorations.

1. Introduction

In dentistry, zirconia (ZrO_2) allowed the realization of all-ceramic restorations due its high strength and toughness, its biocompatibility, esthetic performance and the ability to manufacture precise and consistent frameworks using computer-aided design and computer-aided manufacturing (CAD/CAM) technology [1–3]. Clinical applications of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) also includes all-ceramic cores, post systems and copings [4,5].

Ceramic restorations are conventionally bonded to the prepared tooth with various luting agents [6]. Unlike traditional silica-based ceramics, zirconia cannot be etched in a simple way with hydrofluoric acid, HF, due to the dense polycrystalline structure of zirconia. In addition, the adhesion performance of using silane coupling agents solely is not satisfactory [7,8]. This said, a tribochemical silica-coating method, which is a widely used surface preparation technique, was proposed [9]. After silica-coating, a hydrolysable and hydrophilic silica layer is created on the zirconia surface and a silane coupling agent could be used to mediate bonding [9]. However, the hydrolytic stability of zirconia–resin composite bonding using such a system is still a clinical concern. In the humid and hostile oral environment, clinical longevity could be reduced by the cleavage of the siloxane bonds by water molecules [9]. A recent laboratory study revealed that applying a commercial silane the shear bond strength between zirconia and resin composite significantly reduced when subjected for 8000 thermo-cycles or kept over 4-year in water storage [10]. Even so, another laboratory study [11] suggested that some novel silane systems with blended silanes could yield a better resin zirconia bond performance that might improve the hydrolytic stability. Therefore, a change of the coupling agent might be a key to promote better adhesion.

Other silane [12] and phosphate-based coupling agents [13,14] have also been suggested and attempted to promote adhesion of zirconia restorations to tooth tissues. The suggested mechanism for these coupling agents includes surface wettability, restrained layer theory and chemical binding theory. For example, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) has gained an increasing attention as a monomer alternative to silane coupling agents due to its enhanced bonding and hydrolytic stability [13]. However, this is controversial as some studies showed opposing findings associated with the hydrolytic stability when specimens were artificially aged [15]. Furthermore, it has been suggested that the phosphate ester group from MDP has a strong chemical affinity for the surface layer of zirconia [16]. Surface treatments and activation further increased the durability of the bonding [16].

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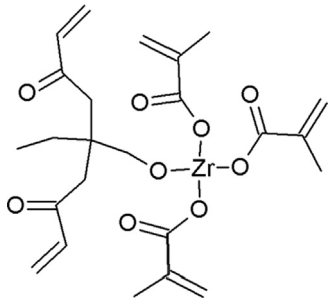

Fig. 1. Chemical structure of zirconate coupling agent Zirconium IV 2,2(bis-2-propenolatomethyl)butanolato, tris 2-methyl-2-propenoato-O (NZ-33).

Zirconate coupling agents have been suggested as an alternative to silane coupling agents. However, limited information regarding the detailed effects has been reported [14,17,18]. It appears promising that a tribochemical treatment and a zirconate coupling agent can obtain better, more durable bonding between resin composites and Y-TZP. One of the zirconate coupling agents is zirconium(IV)-2,2 (bis-2-propenolatomethyl)butanolato-tris 2-methyl-2-propenoato-O (CAS # 153590-16-0), which in this presentation will be referred to by using its trade name NZ-33 (Ken-React® NZ® 33; Kenrich Petrochemicals, Inc., USA). This compound has the tetravalent Zr which is attached to a neopentyl(diallyl)oxy functional group and a trimethyacrylate group (Fig. 1). The hydrophobic trimethacrylate groups are postulated to react with the methacrylate groups of resin composites. The hydrophilic alkoxy groups are presumed to hydrolyze and adsorb onto the zirconia surface. Zirconate coupling agents claim to maintain their coupling capability even in the presence of water [19]. Zirconate compounds have been used to improve the adhesion between inorganic fillers and the organic matrices of a composite material. In particular, an addition of 0.1–1 wt% of the neoalkoxy coupling agent may be mixed into the resin composite material [19]. The presence of the neoalkoxy coupling agents has a plasticizing effect on the resin composite. Interestingly, preliminary cell culture tests have shown that some of these neoalkoxy zirconate coupling agents are not cytotoxic to human osteoblastic-like cells [20,21]. Therefore, the use of neoalkoxy zirconate coupling agents might be viable and feasible in future research, at least in helping the development of chemical binding between the zirconia substrate and the resin composite.

The purpose of this *in vitro* study was to evaluate the effect of a zirconate coupling agent treated with tribochemical coated Y-TZP on flowable resin composite bonding. The outcome, if positive, might be used as reference for clinical cementation of Y-TZP restorations. The hydrolytic stability of this bond was verified after storage while the interface chemistry was evaluated using energy dispersive x-ray (EDX) analysis. The hypotheses were: (1) the modified surface would promote higher and more stable shear bond strength than a surface treated with tribochemical coating only and (2) the modified surface would retain its bond strength after artificial aging.

2. Materials and methods

The schematic test protocol for this study is shown in Fig. 2.

2.1. Zirconia surface substrate preparation

Y-TZP (Upcera Dental Zirconia Blank U98-10W52, Liaoning Upcera, Liaoning, PR China) was used as the substrate for the bonding experiments. Specimens were cut from pre-sintered circular blanks using a band saw. The specimens were polished with 320-grit silicon carbide paper. The specimens were cleansed

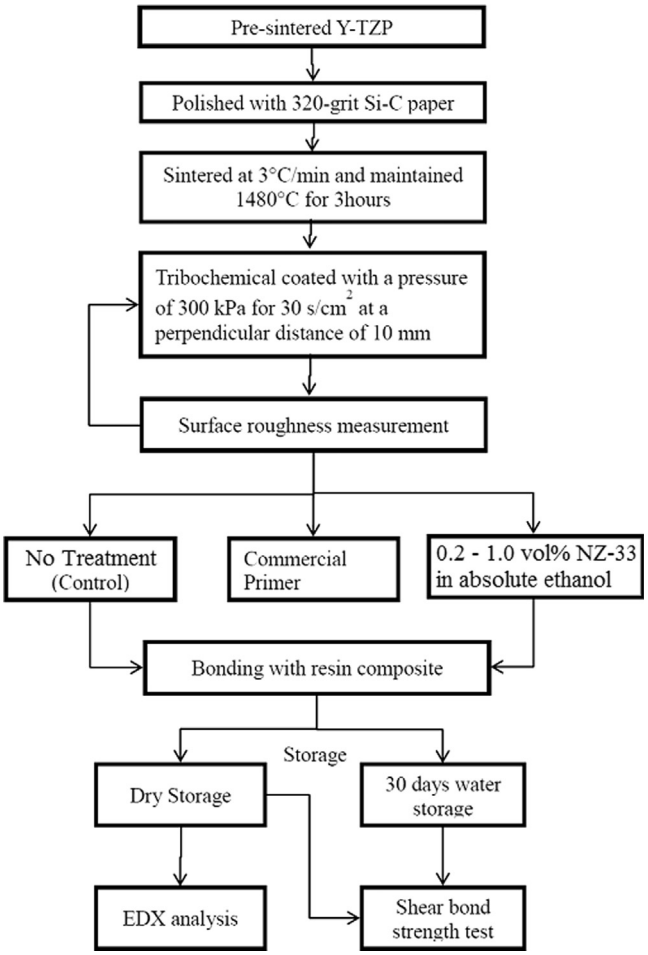

Fig. 2. Schematic test protocol for the current study.

ultrasonically (DFS200, Decon Ultrasonics, Hove Sussex, England) in 70% ethanol (BDH Reagents & Chemicals, Chicago, USA), for 10 min, and then air dried at room temperature. The specimens were sintered in a furnace at a rate of 3 °C/min and maintained at 1480 °C for 3 h according to the manufacturer's specifications. The fully sintered specimens were approximately of the size 8 mm × 6.5 mm × 39 mm. One of the surfaces of a fully sintered specimen was tribochemically silica-coated using 110 μm silica-coated alumina powder, Rocatec® Plus (3M ESPE, Seefeld, Germany), and a sandblasting device. The operating pressure used was 300 kPa and for 30 s/cm^2 and carried out at a constant perpendicular distance of 10 mm. The sandblasted specimens were cleansed with ethanol and air dried at room temperature as described above. The surface roughness (R_a) was then measured using an electro-mechanical profilometer (Surtronic 3+, Taylor Hobson, Leicester, England). Three parallel readings were taken at randomly selected regions of the surface.

2.2. Surface treatment

Prior to the bonding procedure the surfaces were either left untreated, treated with a commercially available phosphate-based primer (Metal/Zr Primer, Ivoclar Vivadent, Schaan, Liechtenstein) or the neoalkoxy zirconate coupling agent zirconium(IV)-2,2(bis-2-propenolatomethyl)butanolato-tris 2-methyl-2-propenoato-O (NZ-33). A total of 7 test groups were used in this experiment. The neoalkoxy zirconate agent was diluted at the concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 vol% in absolute ethanol (99.9–100%