Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of Prosthodontic Research 57 (2013) 88–92

Journal of Prosthodontic Research

www.elsevier.com/locate/jpor

Original article

Comparison of four silane primers and an isocyanate primer for bonding of tri-*n*-butylborane resin to a leucite-reinforced glass ceramic

Yohsuke Taira DDS, PhD*, Miyuki Sakai DDS, PhD, Kohyoh Soeno DDS, PhD,
Takashi Sawase DDS, PhD

Department of Applied Prosthodontics, Graduate School of Biomedical Sciences, Nagasaki University, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan

Received 24 May 2012; received in revised form 5 August 2012; accepted 10 September 2012

Abstract

Purpose: The purpose of the present study was to compare the effectiveness of an isocyanate monomer and four different silane monomers as primer components for bonding a leucite-reinforced glass ceramic (GN-Ceram Block).

Methods: Four different methyl-methacrylate based primers, each with three different concentrations (1, 4, or 16wt%) of 2-methacryloxyethylisocyanate (MOI), 3-methacryloxypropylmethyldimethoxysilane (MDS), 3-methacryloxypropyltrimethoxysilane (MTS), and 3-acryloxypropyltrimethoxysilane (ATS) were prepared. A commercially available silane primer (ESPE^{TM}Sil) was also used as a control. The GN-Ceram Block specimen was ground with silicon carbide paper, rinsed, primed, and then bonded to a resin composite disk using a tri-*n*-butylborane-initiated self-curing luting agent. After 24-h immersion in water, the shear bond strengths were determined.

Results: The highest level of bond strength was obtained with 4wt% MTS (45.2 MPa) and 4wt% ATS (38.7 MPa), followed by 4wt% MOI (29.8 MPa), ESPE^{TM}Sil (28.1 MPa), and 4wt% MDS (27.9 MPa). For each MTS, ATS, MOI, and MDS, the bond strengths for concentrations of 4wt% and 16wt% were not significantly different. No significant differences were found between 4wt% ATS, 4wt% MOI, ESPE^{TM}Sil, and 4wt% MDS. The use of any of these primers led to a significant increase in bond strength compared to an unprimed control (13.8 MPa).

Conclusions: The type and concentration of monomers dissolved in the primer influence the bond strength between a tri-*n*-butylborane resin and a leucite-reinforced glass ceramic GN-Ceram Block. The effectiveness of MOI was found to be comparable to that of MDS, ATS, and ESPE^{TM}Sil, but inferior to that of MTS.

Keywords: Adhesion; Ceramics; Surface modification

---

1. Introduction

Leucite-reinforced glass ceramics are used for dental restorations to satisfy the esthetic demands of patients [1,2]. Full contour crowns including occlusal surfaces can be fabricated from leucite-reinforced glass ceramic blocks by means of computer-aided design and manufacturing (CAD/CAM) systems, such as Aadva (GC Corp., Tokyo, Japan), GN-I (GC Corp.), and ProCAD (Ivoclar Vivadent, Lichtenstein).

Adhesive bonding between the ceramic materials and a resin is a prerequisite for generating a retention force on abutment teeth in order to prevent ceramic fracture, and occasionally for repairing fractured ceramic restorations [3]. In the last half-century, several types of silane compounds have been evaluated as a means of improving ceramic bonding systems. The incorporation of a silica powder treated with tris(2-methoxyethoxy) vinylsilane into an organic polymer reinforced the physical properties of the resin composite [4]. It is well known that 3-methacryloxypropyltrimethoxysilane (MTS) promotes the bonding of the resin to porcelain [5–8]. 1-methacryloxymethyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane (ATS), 3-methacryloxypropyltrichlorosilane, 3-(4-methacryloxyphenyl)propyltrichlorosilane, and a combination of 3-methacryloxypropylsilyltriisocyanate and 3-mercaptopropyltrimethoxysilane have also been evaluated as adhesion promoter [9–11]. Although the authors previously reported that a methylmethacrylate-based primer containing 2wt% MTS was superior to a primer containing 2wt% 3-methacryloxypropylmethyldimethoxysilane, 2wt% 3-methacryloxypropylmethyldiethoxysilane, 2wt% 3-methacryloxypropyltriethoxysilane, or 2wt% ATS [12], only limited information is available regarding the effect of the silane concentration on bonding.

---

* Corresponding author. Tel.: +81 95 819 7688; fax: +81 95 819 7689.
E-mail address: yohsuke@nagasaki-u.ac.jp (Y. Taira).

1883-1958/$ – see front matter © 2012 Japan Prosthodontic Society. Published by Elsevier Ireland. All rights reserved.
http://dx.doi.org/10.1016/j.jpor.2012.09.002

Table 1
Substrate materials, luting agent and primers used in the present study.

Material name	Composition	Manufacturer	Lot no.
Substrate material			
GN-Ceram Block	Silicon dioxide, aluminum oxide, potassium oxide	GC Corp., Tokyo, Japan	0809121
Clearfil DC Core Automix	Bis-GMA, TEGDMA filler (barium glass, silicate glass) photoinitiator, chemical initiator	Kuraray Noritake Dental Inc., Tokyo, Japan	0142AA
Luting agent			
MMA–TBB resin	MMA	Wako Pure Chemical Ind. Ltd., Osaka, Japan	TWQ5264
	Super-Bond C&B activator: tri-*n*-butylborane	Sun Medical Co. Ltd., Moriyama, Japan	RR22
	Super-Bond C&B polymer clear: PMMA powder	Sun Medical Co. Ltd.	RR11
Primer			
MOI primer	1, 4, 16wt% MOI	Showa Denko K.K., Tokyo, Japan	9X152781
	MMA	Wako Pure Chemical Ind. Ltd.	TWQ5264
MDS primer	1, 4, 16wt% MDS	Shin-Etsu Chemical Co., Tokyo, Japan	904346
	MMA	Wako Pure Chemical Ind. Ltd.	TWQ5264
MTS primer	1, 4, 16wt% MTS	Shin-Etsu Chemical Co.	907402
	MMA	Wako Pure Chemical Ind. Ltd.	TWQ5264
ATS primer	1, 4, 16wt% ATS	Shin-Etsu Chemical Co.	909301
	MMA	Wako Pure Chemical Ind. Ltd.	TWQ5264
ESPE^{TM}Sil	1% silane compound Ethanol	3M ESPE AG, Seefeld, Germany	409247

MMA: methyl methacrylate; PMMA: poly(methyl methacrylate); MOI: 2-methacryloxyethylisocyanate; MDS: 3-methacryloxypropylmethyldimethoxysilane; MTS: 3-methacryloxypropyltrimethoxysilane; ATS: 3-acryloxypropyltrimethoxysilane.

On the other hand, there have been some reports on the use of isocyanate monomers, possessing a polymerizable double bond and an isocyanate group, as adhesive monomers for dental adhesives [13–15]. 2-methacryloxyethylisocyanate (MOI) and m-isopropenyldimethylbenzyl isocyanate have been applied as adhesives to bone, dentin, and soft tissue [16,17]. The isocyanate group reacts with active hydrogen or hydroxyl groups, the latter of which are present on the substrate materials under atmospheric exposure. However, no information is available on whether MOI promotes adhesion between resins and ceramics. In addition, there have been no enough attempts to modify the surface of ceramics using isocyanate monomers.

The purpose of the present study was to evaluate the effectiveness of a primer containing MOI and four different primers containing silane monomers in terms of the bond strength between a tri-*n*-butylborane-initiated self-curing luting agent and a leucite-reinforced glass ceramic.

2. Materials and methods

2.1. Materials

The substrate materials, luting agent, and primers used are summarized in Table 1. GN-Ceram Block (GC Corp.) and a resin composite (Clearfil DC Core Automix, Kuraray Noritake Dental Inc., Tokyo, Japan) were used as the substrate materials. GN-Ceram Block consists of 59–60wt% SiO_2 and other oxides (Al_2O_3, K_2O, Na_2O, and CaO), and the fraction of the leucite crystalline phase ($K_2O{\bullet}Al_2O_3{\bullet}4SiO_2$) is 71wt% [2]. The luting agent was a self-curing unfilled resin (MMA–TBB resin) containing methyl methacrylate (MMA) and tri-*n*-butylborane (TBB), but no functional monomer. A total of 12 experimental primers containing 1, 4, or 16wt% of MDS, MTS, ATS, or MOI were prepared, in addition to a commercially available primer (ESPE^{TM}Sil). All of the primers were single-bottle type primers. The structural formulae for MOI and the silanes used in the experimental primers are shown in Fig. 1.

2.2. Specimen preparation

A total of 84 rectangular specimens (8.0 mm × 7.0 mm × 3.0 mm thickness) were cut from the GN-Ceram Block using a high-speed air turbine and a diamond point (Smooth Cut AR15, GC Corp.). The surfaces of the specimens were ground using #600 grit silicon carbide abrasive paper and were then cleaned with water. A 40wt% phosphoric acid aqueous solution was applied to the specimen surfaces for 5 s followed by rinsing in water for 15 s. 1 μL of each primer was applied to the specimens using a micropipette (Eppendorf AG, Hamburg, Germany). In addition, a total of 84 disk-shaped specimens (diameter, 7.0 mm; thickness, 3.0 mm) were fabricated by polymerizing Clearfil DC Core Automix resin in a silicon mold (inner diameter, 7.0 mm; thickness, 3.0 mm) using a light-curing apparatus (α-Light II, J. Morita Corp., Tokyo, Japan) for 180 s.

A 50-μm-thick piece of polyester tape with a circular hole 4 mm in diameter was attached to the rectangular specimens to define the bonding area (Fig. 2). The specimens were bonded to the resin composite disk with MMA–TBB resin using a brush dip technique. The bonded specimens were stored at room temperature for 60 min and were then immersed in water at 37 °C for 24 h before being subjected to shear bond testing.

2.3. Shear bond test

The bonded specimens were embedded in plastic molds using an acrylic resin (Unifast III, GC Corp.). Shear bond strengths were then determined using a shear testing jig (Wago