The application of new adhesive systems to orthodontics and ceramic restorations

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Preface

This thesis is based on the original research works by the author, to which the following articles refer.

Chapter 1. Kitayama S, Nikaido T, Ikeda M, Foxton RM, Tagami J. Enamel bonding of self-etch and phosphoric acid-etch orthodontic adhesive systems. *Dental Materials Journal* 2007;26:135-143.

Chapter 2. Kitayama S, Nikaido T, Maruoka R, Zhu L, Ikeda M, Foxton RM, Tagami J. The effect of pretreatment on bonding of resin cements to zirconia ceramic. (Submitted)

Chapter 3. Kitayama S, Nikaido T, Maruoka R, Zhu L, Ikeda M, Akihiko Watanabe, Foxton RM, Miura H, Tagami J. Effect of an internal coating technique on tensilebond strengths of resin cements to zirconia ceramics. *Dental Materials Journal* (in press)

Chapter 4. Kitayama S, Nikaido T, Zhu L, Ikeda M, Foxton RM, Miura H, Tagami J. The effects of an internal coating technique and silane coupling agents on tensile bond strengths of a resin cement to zirconia ceramics. (Submitted)

Chapter 5. Kitayama S, Foxton RM, Nasser A, Bravis T, Pilecki P, Wilson RF, Nikaido T, Tagami J, Watson TF. Effect of resin coating on adhesion and microleakage of CAD/CAM fabricated all-ceramic crowns after Occlusal loading *in vitro*. (Submitted)

Contents

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Introduction

Since Buonocore (Buonocore, 1955) introduced the acid etch bonding technique in 1955, the bonding of various adhesives to enamel has developed a niche in nearly all areas of dentistry, including restorative dentistry and orthodontics. Orthodontic attachments has been routinely bonded to teeth using the acid etch technique. Its use in orthodontics was pioneered by Newman (Newman, 1965) and later refined by Miura (Miura *et al.*, 1971) at Tokyo Medical and Dental University. Microporosities created during the acid etching process allowed for the incorporation of small resin 'tags' into the enamel surface, thereby creating microscopic mechanical interlocks between the enamel and resin (Buonocore *et al.,* 1968; Gwinnett and Buonocore, 1968; Gwinnett and Matsui, 1967).

The traditional phosphoric acid etch procedure has been used for years to successfully bond orthodontic brackets to teeth. Since the depth of enamel dissolution during the etching process is of clinical importance, the potential use of alternative enamel conditioners, which were initially developed for use on dentin, has been studied in order to improve the bonding procedure by minimizing enamel loss and reducing chair time while still maintaining sufficient bond strengths between the brackets and enamel (Bishara *et al*, 1998; Barkmeier and Erickson, 1994; Triolo *et al.*, 1993). However, little information is available on the effectiveness of the orthodontic adhesives used especially among Japanese orthodontists.

In restorative dentistry, the introduction of zirconia frameworks opened up the design and application limits of all-ceramic restorations with more success and reliability. Nowadays, long span and complex all-ceramic restorations are possible due to the unique and excellent mechanical properties of zirconia (Aboushelib *et al.*, 2006).

Due to their high fracture resistance, zirconium-oxide crowns and FPDs can be cemented using conventional methods recommended by the manufacturers. However, resin bonding between a tooth and the restoration is advocated for improving the retention, marginal adaptation, and fracture resistance of restorations (Burke *et al*, 2002;

Rosenstiel *et al.*, 1998). Although hydrofluoric acid etching and the application of a silane coupling agent to silica-based ceramics increases the bond strength between all-ceramic restorations and composite resins (Ozcan and Vallittu, 2003; Della Bona *et al.*, 2002), these techniques do not improve the bond strength of zirconium and alumina ceramics because their high crystalline content makes them resistant to acid etching (Derand and Derand, 2000; Yoshida *et al., 2004*).

Clinically cement selection is a prerequisite for ensuring effective bond strength to zirconia. In addition, the promising surface treatment of zirconia surface should be established.

In the early 90s, a resin coating technique was introduced for indirect restorations to minimize pulpal irritation and postoperative sensitivity (Nikaido *et al.*, 1997; Momoi *et al.*, 2003). This technique also enables better bonding, sealing, and adaptation to dentin (Peters and McLean, 2001). Resin coating in combination with a dentin adhesive system and a low-viscosity microfilled resin has been recommended for the prepared cavity immediately after tooth preparation, just before taking a final impression.

This technique may also be applicable to CAD/CAM all-ceramic restorations including the CEREC system, which offers the dentist the opportunity to prepare, design and fabricate a ceramic restoration in a single appointment, without the need for making impressions, provisional restorations or dental laboratory support (Mormann *et al.*, 1987).

Bond strength and leakage studies have been used individually as in vitro indicators of both retention and marginal sealing abilities of composite restorations. However, to the authors' knowledge, no information is available regarding the effect of resin coating and occlusal loading on the adhesion and microleakage of all-ceramic crowns fabricated with CEREC 3.

Chapter 1 investigated the effects of self-etch and phosphoric acid-etch orthodontic adhesives on enamel bonding in terms of bond strength and the morphology. A newly developed self-etch adhesive was compared with conventional phosphoric

acid-etch adhesives.

Chapter 2 evaluated the bond strength of five resin cements to zirconia and silica-based ceramics using six primers in order to screen the effectiveness of resin cements and primers.

Based on the results of Chapter 2, **Chapter 3** investigated the effect of the coating of the zirconia surface by fusing a silica-based ceramic in order to enhance the bonding of resin cement to zirconia. This coating would be applied to the internal surface of the zirconia restoration clinically.

Based on the results of Chapter 2 and 3, **Chapter 4** evaluated the effects of the coating technique of the zirconia surface on bonding durability of resin cement to zirconia with different silane coupling agents.

Chapter 5 investigated the effect of resin-coating and occlusal-loading on the microleakage and microtensile bond strength of CAD/CAM fabricated all-ceramic crowns cemented with a resin cement. In this study, a self-etching, one-bottle bonding agent, Clearfil Tri-S Bond, was used as a resin coating material.

Chapter 1

Enamel bonding of self-etch and phosphoric acid-etch orthodontic adhesive systems

Introduction

Phosphoric acid etching of enamel was introduced by Buonocore in 1955 (Buonocore, 1995), which has since led to dramatic changes in the practice of orthodontics (Zarrinnia *et al.*, 1995). By the 1970s, the bonding of orthodontic brackets had become an accepted clinical technique (Thanos *et al.*, 1979; Gorelick, 1977). Bonded orthodontic brackets have advantages over bands in that they have no interproximal contacts, are easier to place and remove, are more esthetic, hygienic, and less irritating to the gingival (Proffit, 1986).

However, the components of the appliance and the bonding materials often promote plaque accumulation with subsequent acid production, leading to decalcification and an alteration in the appearance of the enamel surface (O'Reilly and Featherstone, 1987).

Although the acid etching technique is a useful procedure in orthodontics, there is a need to improve the bonding procedure for two key reasons: to maintain clinically useful bond strengths while minimizing the amount of enamel loss, and to simplify the technique by reducing the number of steps.

Bonding systems used in operative dentistry were developed to combine conditioning and priming agents into a single acidic primer for simultaneous use on enamel and dentin, eliminating the separate steps of etching, rinsing, and drying (Chigira *et al.*, 1989; Han *et al.*, 2004). The use of a self-etching primer offers the advantage of a faster and simplified application technique, thereby allowing adequate etching and priming of enamel and dentin in only one step (Cacciafesta *et al.*, 2003). In

addition to saving time, fewer steps in the bonding process might translate into fewer procedural errors, thus minimizing technique sensitivity.

A self-etching primer system has been introduced for the bonding of orthodontic brackets (Sirirungrojying *et al.*, 2004). Bishara *et al.* (Bishara *et al*, 2001) reported that the use of a self-etching primer system resulted in a clinically acceptable bond strength.

Recently, a new orthodontic adhesive, Beauty Ortho Bond (Shofu, Kyoto, Japan), was developed, which is composed of a self-etching primer and a fluoride-releasing adhesive system.

The purpose of this study was to examine the shear bond strengths of self-etch and phosphoric acid-etch orthodontic adhesive systems to enamel. In addition, the modes of bracket failure were examined using scanning electron microscopy (SEM).

Materials and Methods

Materials used in this study

The materials used in this study are listed in Table 1. Two self-etch adhesive systems, Beauty Ortho Bond (BO, Shofu, Kyoto, Japan) and Transbond XT (TB, 3M Unitek, Monrovia, CA, USA), and two phosphoric acid-etch adhesive systems, Kurasper F (KF, Kuraray Medical, Tokyo, Japan) and Orthomite Superbond (OS, Sun Medical, Moriyama, Japan), were used in this study.

Beauty Ortho Bond is composed of a self-etching primer and a fluoride-releasing light-cured adhesive system. The primer includes a phosphonic acid monomer, which contributes to etching enamel. The adhesive paste includes S-PRG (surface pre-reacted glass ionomer) filler particles, which are formed by an acid-base reaction between fluoroaluminosilicate glass and a polyalkenoic acid in the presence of water (Ikemura *et al.*, 2003). S-PRG fillers can release and recharge fluoride ions (Ikemura *et al.*, 2003).

Table 1 Materials used in this study

Material	Manufacturer	Batch No.	Composition	Instructions
Beauty Ortho Bond (BO)	Shofu, Kyoto, Japan	Primer A: 11031301	Water, Solvent	3s apply
		Primer B: 03041101	Phosphonic acid monomer, Solvent, Dyes	Gently air-dry
		Paste: 02040901	TEGDMA, S-PRG filler, Bis-GMA	20s light-cure
Transbond XT (TB)	3M Unitek, Monrovia, CA, USA	Transbond Plus self-etching primer: 204758	Methacrylated phosphoric acid esters, Amino benzoate, Camphorquinone, Others	3s apply Gently air-dry
		Paste: 5MU	Bis-GMA, TEGDMA, Silane-treated quartz, Amorphous silica, Camphorquinone	20s light-cure
Kurasper F (KF)	Kuraray Medical, Tokyo, Japan	K-etchant: 00353B	37% Phosphoric acid	40s apply, 20s wash Strongly air-dry
		F-bond: 00036B	TEGDMA, 2-HEMA, Bis-GMA, Methylmethacrylate-methacryloyl fluoride copolymer, Sodium fluoride, Silanated silica filler, Initiators	
		Paste: 00026F	TEGMA, Bis-GMA, Silanated glass filler, Initiators	40s light-cure
Orthomite Superbond (OS)	Sun Medical, Moriyama, Japan	Red Activator: LE4	65% Phosphoric acid	30s apply
		Powder: KX2	PMMA	20s wash
		Liquid: LF3	MMA, 4-META	Strongly air-dry
		Catalyst: LE61	Tri-n-butylborane	Chemical-cure

TEGDMA: triethylene glycol dimethacrylate; PRG: pre-reacted glass ionomer; Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; MMA: methyl methacrylate; PMMA: polymethyl methacrylate; 4-META: 4-methacryloyloxyethyl trimellitate anhydride

Transbond XT is composed of a fluoride-free light-cured adhesive system. Transbond Plus self-etching primer was used as a conditioner, which contains methacrylated phosphoric acid esters.

Kurasper F is composed of a phosphoric acid etchant and a fluoride-releasing light-cured adhesive system in which sodium fluoride is the source of fluoride ion release.

Orthomite Superbond is composed of a phosphoric acid etchant and a fluoride-free chemically cured adhesive system which consists of PMMA powder, a liquid component (MMA and 4-META), and a chemical initiator (tri-n-butylborane) (Kameyama *et al.*, 2003; Hirabayashi, 2003).

Specimen preparation

Eighty freshly extracted bovine incisors free of obvious defects were stored frozen prior to use. The roots of the teeth were cut off, leaving the crowns, which were embedded in a chemically cured acrylic resin (Unifast Trad; GC, Tokyo, Japan) in an acrylic tube to allow for standardized and secure placement during testing. The facial enamel surface was parallel to and about 1 mm above the cylinder rim. Then, the exposed enamel was flattened with 600-grit silicone carbide paper under copious water to provide an area for bonding. The enamel surfaces were then cleaned ultrasonically in distilled water. After which, the specimens were randomly divided into eight groups.

Orthodontic metal brackets (One Piece Bracket; Kanno, Nagareyama, Japan) with a bonding area of 16.96 mm^2 were bonded to the enamel surface according to the manufacturers' instructions (Table 1).

All bonding procedures were performed by the same operator. Excess adhesive was carefully removed, and the BO, TB, and KF specimens were light-cured with a visible light curing unit (Optilux 500; Sybron Kerr Corp., USA), while the specimens of OS were chemically cured at room temperature. For BO and TB, the specimens were light-cured for 20 seconds (10 seconds from the mesial edge and 10 seconds from the

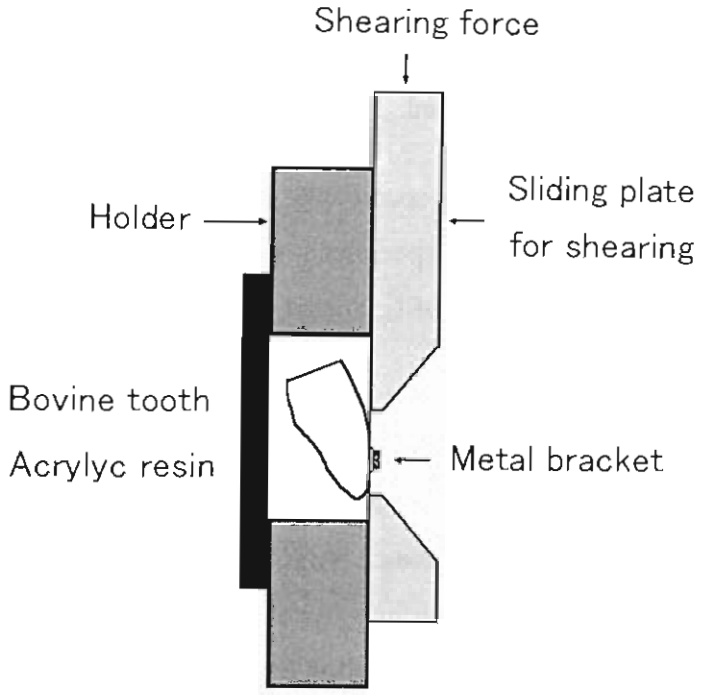
distal edge of bracket). For KF, the specimens were light-cured for 40 seconds (20 seconds from mesial and 20 seconds from distal).

Shear bond test

Prepared specimens were left at room temperature for 30 minutes, and then stored in one of the two conditions as follows: deionized water at 37°C for 24 hours (TC-0) or deionized water at 37°C for 24 hours followed by thermal cycling of 5000 times (5–55°C, dwell time of 30 seconds each) (TC-5000). Thermal cycling is a well-known *in vitro* durability test, which accelerates water penetration through the interface between the adhesive and enamel. Bishara *et al.* (Bishara *et al*, 2003) evaluated the bonding durability of orthodontic brackets using thermal cycling of 500 times. Sirirungrojying *et al.* (Sirirungrojying *et al.*, 2004) also evaluated bonding durability using thermal cycling of 2000 and 5000 times. In this study, thermal cycling was determined at 5000 times.

Shear bond test was performed for each specimen using an ISO standard jig (Noguchi *et al.*, 1982) in the same manner as described by Ikeda *et al.* (Ikeda *et al.*, 2005). A universal testing machine (AG–500B, Shimadzu, Kyoto, Japan) was used for the shear bond test at a crosshead speed of 1 mm/min as shown in Fig. 1. Each tooth was oriented so that its facial surface was parallel to the direction of force during the shear bond test. The force was directly applied to the bracket-tooth interface. Load at bracket failure was recorded by a personal computer connected to the testing machine. Shear bond strength value was calculated in MPa by dividing the force by the area of the bracket base.

Figure 1. Schematic drawing of shear bond strength measurement.



Failure mode analysis

After debonding, the teeth and brackets were examined under x10 magnification with an optical microscope (OME-GWHIO; Olympus Co., Tokyo, Japan) and scored according to the criteria of the adhesive remnant index (ARI) (Artun and Bergland, 1984) as follows: 0 – No adhesive left on tooth; 1 – Less than half of the adhesive left on tooth; 2 – More than half of the adhesive left on tooth; 3 – All the adhesive left on the tooth, with distinct impression of the bracket mesh.

SEM observation

The ground enamel surface and enamel surfaces conditioned with each adhesive system were observed with an SEM. The enamel surface was ground with 600-grit silicone carbide paper under copious water and ultrasonically cleaned in distilled water. For BO and TB, the self-etching primer of each system was applied to the ground enamel

surface according to the manufacturers' instructions, gently air-blown, rinsed with acetone for 30 seconds, and then rinsed with distilled water for 30 seconds followed by gentle air-drying. For KF and OS, the enamel surface was etched with phosphoric acid, rinsed with water for 30 seconds, and gently air-dried.

To observe the debonded surface of the specimens, representative debonded specimens were selected from each group. All specimens were gold sputter-coated before examination with a SEM (JSM–5310LV; JOEL, Tokyo, Japan).

Statistical analysis

The number of specimens per group for shear bond testing was ten. Shear bond strengths were analyzed by two-way analysis of variance (ANOVA) using the Statistical Package for Medical Science (SPSS Ver.11 for Windows) for statistical procedures. The factors analyzed were material and storage condition. Following this, Tukey's HSD test was performed. ARI scores of the mode of failure were analyzed using Steel-Dwass nonparametric multiple comparison test by Tukey's procedure. The statistical calculations of mode of failure were performed using a statistical software, KyPlot (Version 3.0 for Windows, Keyence Incorporated, Tokyo, Japan). Significance for all statistical tests was predetermined at a 95% confidence level.

RESULTS

Shear bond strength

The shear bond strengths of the four orthodontic adhesives to enamel are summarized in Table 2. Statistical significance of the bond strengths to enamel is shown in Table 3. Two-way ANOVA revealed that bond strength was influenced by both material ($F=4.688$, $p=0.005$) and storage condition ($F=21.720$, $p=0.0001$). There was also a significant interaction between the independent variables, material and storage condition ($F=3.272$, $p=0.026$).

In the TC-0 groups, there were no significant differences between BO and phosphoric acid-etching adhesive systems (KF and OS), while the bond strength of TB was significantly lower than those of phosphoric acid-etching adhesive systems (KF and OS). There were no significant differences between BO and TB, and between KF and OS, respectively ($p>0.05$).

Table 2 Shear bond strengths to enamel (MPa)

	TC-0	TC-5000
BO	20.3 ± 4.7	18.8 ± 4.1
TB	17.6 ± 4.0	16.4 ± 3.3
KF	23.9 ± 3.8	17.5 ± 4.9
OS	24.9 ± 3.2	17.7 ± 2.8

n=10, Mean ± SD, TC-0: Not thermocycled, TC-5000: Thermocycled

In the cases of BO and TB, there were no significant differences in bond strength between TC-0 and TC-5000 ($p>0.05$). However, the bond strengths of KF and OS significantly decreased after 5000 times of thermal cycling ($p<0.05$).

In the TC-5000 groups, there were no significant differences in bond strength among the adhesive materials ($p>0.05$).

Modes of failure

The modes of failure according to the ARI index are summarized in Table 4. For each adhesive, no significant differences were observed between the TC-0 and TC-5000 groups ($p>0.05$). However, there were significant differences in the mode of failure between KF (TC-0) and OS (TC-0), and between KF (TC-5000) and OS (TC-0) ($p<0.05$). The predominant modes of bracket failure for BO, TB and KF were at the

enamel-resin interface with less than 50% of the adhesive on the enamel surface, whereas the bracket-resin interface was the most common site of failure in OS.

Table 3 Summary of the statistical analysis of the bond strengths to enamel using ANOVA supplemented with Tukey's HSD test

		BO		TB		KF		OS	
Adhesive	**TC**	**TC-0**	**TC-5000**	**TC-0**	**TC-5000**	**TC-0**	**TC-5000**	**TC-0**	**TC-5000**
BO	TC-0								
	TC-5000	n.s.							
TB	TC-0	n.s.	n.s.						
	TC-5000	n.s.	n.s.	n.s.					
KF	TC-0	n.s.	n.s.	*	*				
	TC-5000	n.s.	n.s.	n.s.	n.s.	*			
OS	TC-0	n.s.	*	*	*	n.s.	*		
	TC-5000	n.s.	n.s.	n.s.	n.s.	*	n.s.	*	

Table 4 Frequency distribution of adhesive remnant index (ARI) scores

	TC-0				TC-5000			
	ARI scores				ARI scores			
	0	1	2	3	0	1	2	3
BO	3	7	0	0	2	5	1	2
TB	6	3	1	0	4	5	1	0
KF	8	2	0	0	7	3	0	0
OS	1	2	2	5	2	1	2	5

ARI indicates adhesive remnant index; 0: No adhesive left on the tooth; 1: Less than half of the adhesive left on the tooth; 2: More than half of the adhesive left on the tooth; 3: All the adhesive left on the tooth with distinct impression of the bracket mesh.

SEM observation

Figure 2 shows an enamel surface ground with 600-grit silicone carbide paper. A smear layer was created on the ground surface with some scratch lines. On the other hand, the enamel surfaces conditioned with each adhesive are shown in Figs. 3(a) to (d).

The smear layer on the ground enamel was completely removed after conditioning by all the adhesive systems. However, the etched enamel patterns were different between the self-etching primers (Figs. 3(a) and (b)) and phosphoric acid etchants (Figs. 3(c) and 3(d)).

Figure 2 SEM photograph of enamel surface ground with 600-grit silicone carbide paper (x2000). Smear layer and scratch lines were observed.

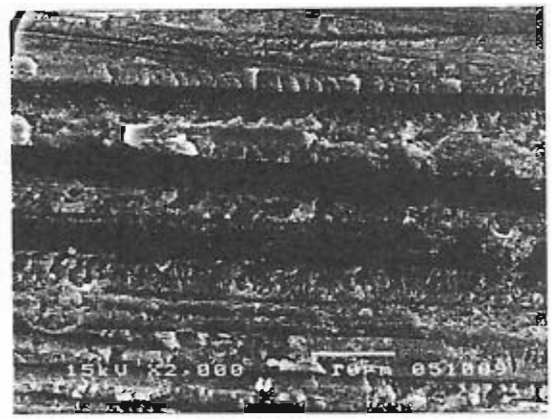


Figure 3 SEM photographs of enamel surfaces conditioned with each adhesive (x7500). a: Beauty Ortho Bond primer; b: Transbond Plus self-etching primer; c: 37% phosphoric acid in Kurasper F; d: 65% phosphoric acid in Orthomite Superbond. Enamel surfaces were slightly roughened by the acidic primer (a, b), while enamel surfaces were strongly etched and the prismatic structure of the enamel surface was selectively etched and easily identified (c, d).

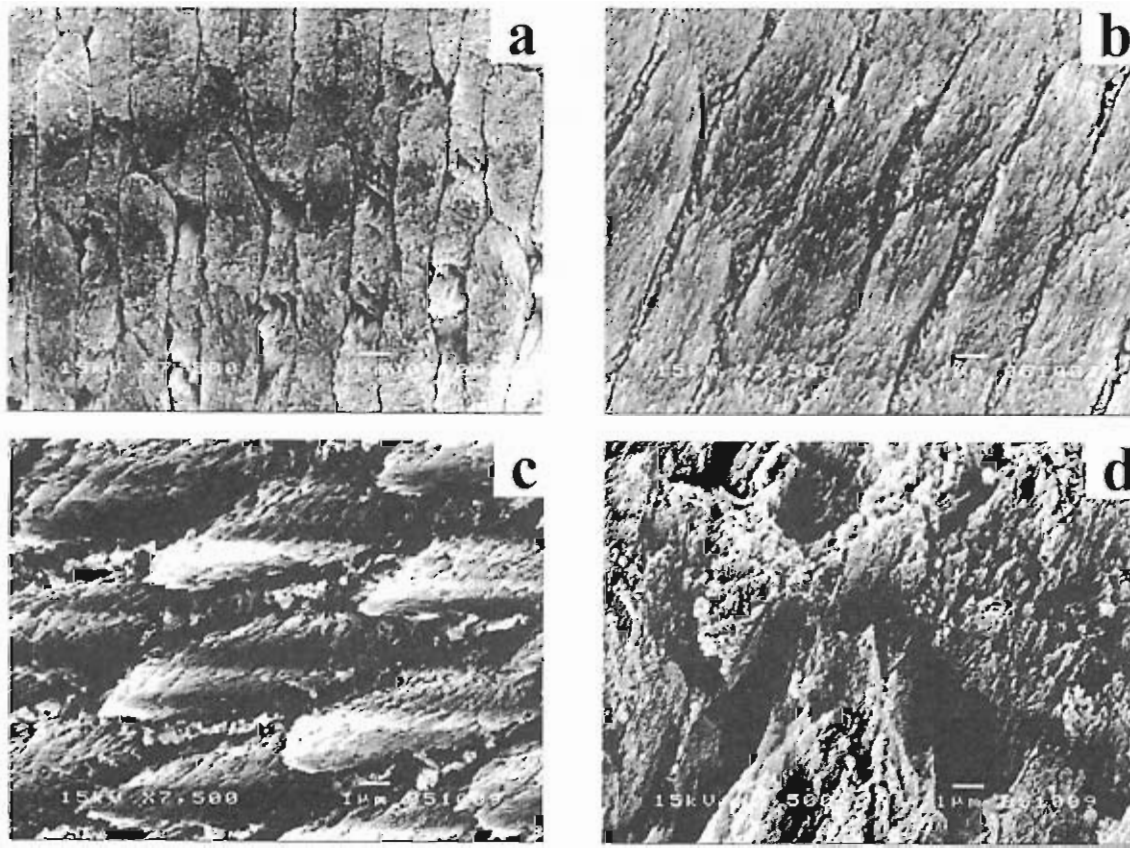
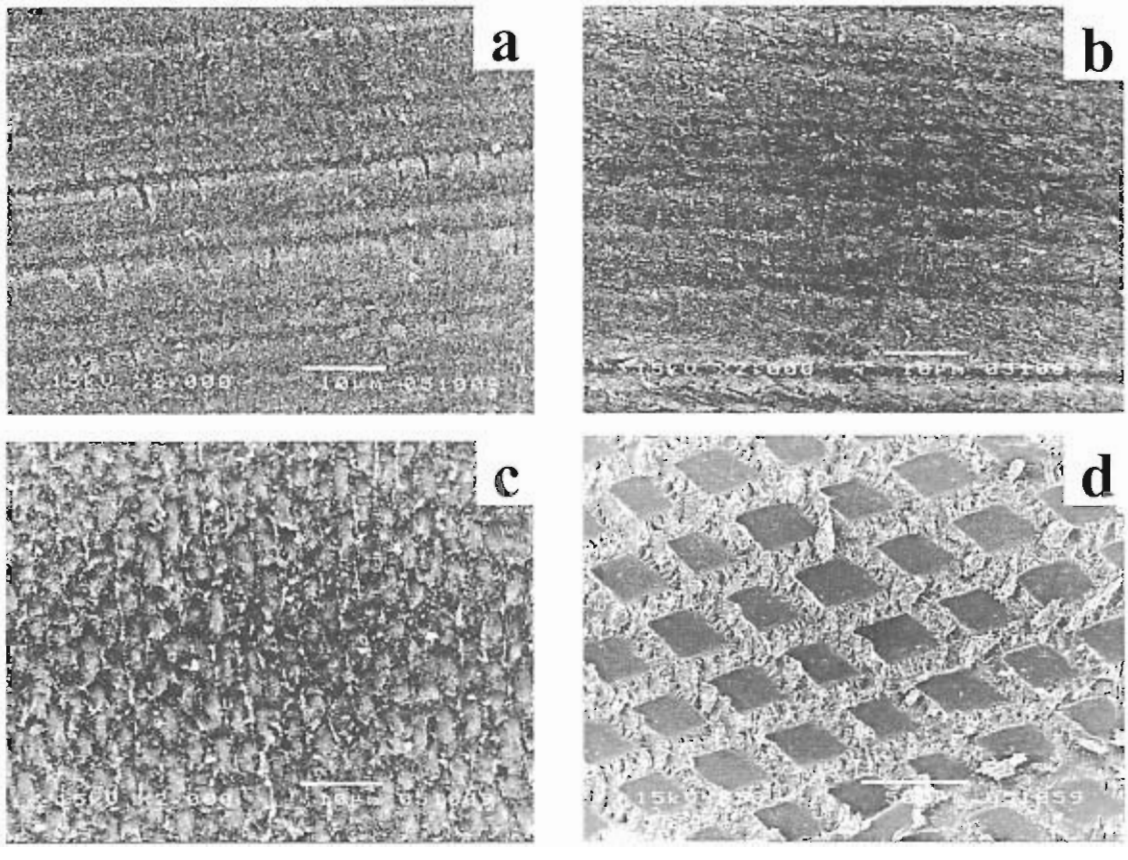


Figure 4 SEM photographs of typical fracture surfaces on the enamel side after shear bond testing. a: Beauty Orthobond (TC-0) (x2000); b: Transbond XT (TC-0) (x2000); c: Kurasper F (TC-0) (x2000); d: Orthomite Superbond (TC-0) (x50). Partial adhesive failure was observed, and remnants of adhesive remained on the enamel surface (a, b, c). Distinct impression of the bracket mesh was observed (d). Mode of fracture tendency of each adhesive was not different between the TC-0 and TC-5000 groups.



DISCUSSION

Direct bonding of orthodontic brackets using the acid-etch technique has become a common technique in the orthodontic field. Phosphoric acid etching produces a roughened enamel surface by dissolving calcium components and forming enamel resin tags. Although enamel etching technique is a useful and accepted procedure for bonding

orthodontic brackets, there is a need to maintain clinically useful bond strengths while minimizing the amount of enamel loss.

Recent studies in operative dentistry have suggested that self-etching primers with lower decalcifying ability are less effective than phosphoric acid etching when used to bond to ground enamel or intact enamel (Pashley and Tay, 2001). Previously, Bishara *et al.* (Bishara *et al.*, 2001) found that the shear bond strength of orthodontic brackets after Prompt L-Pop self-etching primer treatment was significantly lower than that after phosphoric acid etching with TB. Yamada *et al.* (Yamada *et al.*, 2002) also found that the shear bond strength after SE Bond self-etching primer (Kurary Medical) treatment was significantly lower than that after phosphoric acid etching with KF. Similarly, the present study demonstrated that the shear bond strengths of brackets bonded with the self-etching adhesive systems (BO and TB) were lower than those bonded with phosphoric acid-etching adhesive systems (KF and OS) in the control groups. However, a bond strength of approximately 17 MPa was maintained after thermal cycling in the self-etching adhesive groups, while the bond strength significantly decreased after thermal stress in the phosphoric acid-etching groups. It should be pointed out that Martin and Garcia-Godoy (Martin and Garcia-Godoy, 1994) commented that high shear bond strength in orthodontics is not necessarily a beneficial property of an orthodontic adhesive, because enamel can be lost during the debonding procedure as well as during the removal of residual resin. Bishara *et al.* (Bishara *et al.*, 1999) reported that a shear bond strength of 7 MPa to the enamel was clinically acceptable for bonding to the enamel surface in orthodontic treatment. Data obtained in this study thus suggested that all the adhesive systems evaluated were acceptable for routine clinical use.

The effects of thermal changes on the bond strength of resin-based materials to hard dental tissues, as well as on their mechanical properties (*i.e.*, fracture toughness, elastic modulus), have been well documented (Miyazaki *et al.*, 2000; Price *et al.*, 2003). Thermal cycling stresses the bond between resin and tooth substance and might affect bond strength (Nikaido *et al.*, 2002). Christensen (Christensen, 2002) commented that

impressive *in vitro* bond strengths were transient when subjected to temperature changes in the mouth.

In the case of self-etching adhesive systems, the acidic monomers in the self-etching primers are responsible for both etching and bonding. As such, the depth of demineralized enamel corresponds to the depth of penetration of the adhesive to be polymerized. This mechanism thus circumvents problems associated with insufficient penetration as well as improves the quality of hybridization (Weerasinghe *et al.*, 2005; Nakabayashi and Pashley, 1998; Gordan *et al.*, 1997), thereby ensuing an excellent mechanical lock.

Phosphoric acid etching creates resin tags for mechanical retention between enamel and resin. However, the resin may not completely infiltrate etched enamel (Shinchi *et al.*, 2000). A region of unprotected enamel prisms might be susceptible to hydrolytic degradation after thermal cycling. In addition, water diffusion into the bonded interface between adhesive and tooth surface was found to cause the resin to swell and become plasticized (Soderholm, 1991), as well as reduce enamel hardness due to loss of surface calcium (Muhlemann, 1964).

Basically, there are two opinions on the remaining adhesive following bracket debonding. One opinion largely favors bracket-adhesive interface failure with the adhesive resin left mainly on the enamel surface (Proffit W, 1986; Bishara *et al.*, 2004), when a heavy-filled resin is used to bond orthodontic attachments. The microporosities created by etching are filled with the resin and provide mechanical retention. The second opinion favors failure at the enamel-adhesive resin interface, because there is less adhesive left to remove from the enamel surface after debonding (Bishara *et al.*, 2004). Martin and Garcia-Godoy (Martin and Garcia-Godoy, 1994) suggested that a weaker adhesive with a lower strength value might be preferable so as to increase failure rate at the enamel-adhesive resin interface. In this way, minimal clean-up would be needed with reduced likelihood of damage to the enamel.

The predominant mode of bracket failure for BO, TB, and KF was at the enamel-resin interface with less than 50% of the adhesive on the enamel surface. In the cases of BO and TB, scratch lines with 600-grit silicone carbide paper were observed

after debonding, which indicated that the self-etching adhesive systems did not damage the enamel surface during debonding.

As for OS, the predominant mode of bracket failure was at the bracket-adhesive interface with more than 50% of the adhesive on the enamel surface. OS is MMA-based, the mechanical properties of which are weaker than the light-cured adhesive resins (Burrow *et al.*, 1994; Kitasako *et al.*, 2002). Hotta *et al.* (Hotta *et al.*, 1992) reported that 4-MET, a hydrolysis product of 4-META, promoted effective diffusion of monomers into enamel. SEM observations of the conditioned enamel surfaces revealed that the self-etching primers produced less enamel dissolution compared with phosphoric acid etching. Moreover, the morphological appearances of the enamel surface were different between KF and OS, which was probably due to the different concentrations of phosphoric acid in the etchants. The 37% phosphoric acid of K-etchant in KF was more aggressive than the 65% solution of Red Activator in OS (Shinchi *et al.*, 2000).

Decalcification is a common side effect of fixed appliance orthodontic treatment (Millett *et al.*, 1999). On this note, orthodontic treatment with multibonded appliances poses a significant caries risk (O'Reilly and Featherstone, 1987; Ogaard, 1989). To counter this problem, fluoride-releasing composites for bonding brackets have attracted considerable attention and garnered much interest. This is because they may inhibit the decalcification of enamel around the brackets by delivering fluoride to the affected environment (Mitchell, 1992; Cildir and Sandalli, 2005). Furthermore, the remineralization capability and antibacterial property of fluoride may help eliminate the risk of dental caries (Imazato, 2003). BO contains S-PRG filler for the release and uptake of fluoride ions, and might thus prevent demineralization but facilitate remineralization of the surrounding enamel (O'Reilly and Featherstone, 1987).

Orthodontic bracket bonding is performed on intact enamel. The intact enamel surface is hypermineralized and contains more fluoride than ground enamel. Prismless layer on enamel surface (Whittaker, 1982) is less conducive to bonding by conventional acid gel conditioning (Nathanson *et al.*, 1982) and self-etching primer application (Kanemura *et al.*, 1999). Kanemura *et al.* (Kanemura *et al.*, 1999) reported that bond

strength was significantly reduced when self-etching systems were bonded to intact enamel. Similarly, Senawongse *et al.* (Senawongse *et al.*, 2004) reported that self-etching adhesive systems exhibited significantly lower bond strengths than the phosphoric acid-etching adhesive systems on intact enamel. However, no statistically significant differences were found between self-etching adhesive systems and phosphoric acid-etching adhesive systems to ground enamel. Furthermore, bond strengths of self-etching adhesive systems to ground enamel were significantly higher than those to unground enamel, whereas phosphoric acid etching systems showed no such significant differences between intact and ground enamel. Based on the results obtained to date, further research is indeed needed to clarify whether self-etching primer adhesive systems could provide sufficient bond strength to intact human enamel.

CONCLUSIONS

Self-etching adhesives, Beauty Ortho Bond and Transbond XT, showed more stable bond strengths to ground enamel after thermal cycling than the phosphoric acid-etching adhesives, Kurasper F and Orthomite Superbond. In addition, with self-etching adhesives, problems concerning the decalcification of and damage to the enamel surface were eliminated.

CHAPTER 2

The effect of pretreatment on bonding of resin cements to zirconia ceramics

Introduction

The popularity of all-ceramic restorations has increased in recent years due to their superior esthetic appearance and metal-free structure (Blatz *et al.*, 2003). Computer-aided design and manufacturing (CAD/CAM) has become an increasingly interesting alternative to manual, casting, or pressing techniques. The clinical success of glass-infiltrated alumina ceramic (Scotti *et al.*, 1995; Pröbster, 1996; Haselton, 2000) and CAD/CAM-fabricated densely sintered high-purity alumina ceramic (Odén *et al.*, 1998; Odaman and Andersson, 2001) relies on their high flexural strength and fracture resistance compared with other porcelains available (Andersson and Odén, 1993; Castellani *et al.*, 1994; Seghi and Sorensen, 1995; Zeng *et al.*, 1998; Strub and Beschnidt, 1998).

Zirconia is a high flexural strength ceramic (>1000 MPa) (Piconi and Maccauro, 1999), that is about six times stronger than feldspathic porcelains, which has been used as an orthopedic material (Cales *et al.*, 1984). Based on these improved physical properties compared with alumina-based ceramics, zirconia ceramic was introduced to restorative dentistry. Polycrystalline zirconia is typically used in the tetragonal crystalline phase, partially stabilized with yttrium oxide (Y-TZP) (Christel *et al.*, 1989). Clinical applications of Y-TZP include all-ceramic cores and post systems (Meyenberg *et al.*, 1995; Lopes *et al.*, 2001) and as copings for complete coverage all-ceramic crowns and fixed partial dentures (McLaren, 1998; Blatz, 2002).

Along with the strength of the material, the cementation technique is also important for the clinical success of a restoration (Burke *et al.*, 2000; Rosenstiel *et al.*,

1998). Due to their high fracture resistance, zirconium-oxide crowns and FPDs can be cemented using conventional methods recommended by the manufacturers. However, resin bonding between a tooth and the restoration is advocated for improving the retention, marginal adaptation, and fracture resistance of restorations (Burke *et al.*, 2000; Rosenstiel *et al.*, 1998).

Obtaining adhesion between resin cement and a ceramic surface requires surface pretreatment (Ozcan and Vallittu, 2003; Ozcan, 2002). The use of a silane coupling agent is recommended for glasses and porcelains in order to form a siloxane network with the silica in the ceramic surface, to improve the bond strength between the resin cement and the ceramic. However, these techniques do not improve the bond strength of zirconium and alumina ceramics because this chemical reaction is not possible with these ceramics. Also their high crystalline content makes them resistant to hydrofluoric acid etching (Ozcan and Vallittu, 2003; Derand and Derand 2000; Yoshida *et al.*, 2004). For these high strength-ceramics, airborne particle abrasion is an alternative method for roughening the ceramic surface (Kern and Wegner, 1998; Ozcan *et al.*, 2001).

Blatz *et al.* (Blatz *et al.*, 2004) compared the bond strength of different bonding/silane coupling agents and resin cements to zirconium-oxide ceramics. They reported that resin cements containing MDP can bond strongly to sandblasted zirconia.

Recently, a new resin cement and primer for bonding alumina and zirconia ceramics were developed. Therefore, the purpose of this study was to examine the tensile bond strength of five resin cements to zirconium oxide ceramics compared with that to silica-based ceramics. The experimental hypothesis was that pretreatment with primer influenced the bonding of resin cements to zirconia ceramic.

Materials and Methods

The ceramic materials used in this study are shown in Table 1. Seventy-seven silica-based ceramic specimens (GN-1 Ceramic Block; GC, Tokyo, Japan) were obtained from the manufacturer. The dimensions of all the specimens were 13×17×21 mm. Seventy-seven zirconium-oxide ceramic specimens were fabricated from ingots (Cercon Base; Degudent, Hanau, Germany) according to the manufacturer's instructions. The specimens had a diameter of 15 mm and a thickness of 2 mm.

Table 1. Ceramic materials used in this study

Trade name	Composition	Manufacturer
GN-1 Ceramic Block (Batch No. 0507121)	Leucite glass-ceramics	GC, Tokyo, Japan
Cercon Base (Batch No. 18001459)	Zirconium Dioxide: 89.2wt% Yttrium Trioxide: 5.0wt% Hafnium Dioxide: <2.0wt%	Degudent, Hanau, Germany

The resin cement and the primer which come with each resin cement for bonding ceramics used in this study are listed in Tables 2 and 3. The combinations were as follows; Bistite II (BS) and Tokuso Ceramic Primer (Tokuyama Dental, Tokyo, Japan), Linkmax (LM) and GC Ceramic Primer (GC, Tokyo, Japan), RelyX ARC (RX) and RelyX Ceramic Primer (3M ESPE, St. Paul, MN, USA), and Panavia F 2.0 (PF) and Clearfil Ceramic Primer (Kuraray Medical, Tokyo, Japan). For ResiCem (RC), one of two primers; Porcelain Primer (Po) and AZ Primer (AZ, Shofu, Kyoto, Japan) were used in this study.

Tokuso Ceramic Primer and Clearfil Ceramic Primer contain phosphoric acid monomers, while AZ Primer contains the phosphonic acid monomer, 6-MHPA, which was developed for bonding to alumina and zirconia ceramics.

The ceramic surfaces of the specimens were ground up to 600-grit silicon carbide paper in a polishing machine (Ecomet 4; Buehler, Lake Bluff, IL, USA), and then airborne-particle abraded using a sandblaster (Hi Blaster Ovaljet; Shofu, Kyoto,

Japan) with 70-μm Al_2O_3 particles (Hi Aluminas; Shofu, Kyoto, Japan) at 0.5 MPa for 5 seconds at a distance of 10 mm. Then, they were ultrasonically cleaned in water for 10 minutes and air-dried. A piece of polyethylene tape with a circular hole 4.0 mm in diameter was positioned on the surface of the specimen to control the area of bonding. Before bonding, the specimens in each group (n=7) were treated as follows; no pretreatment as a control (-) or conditioned with pimer (+).

Table 2. Resin cements used in this study

Material	Batch No.	Composition	Manufacturer
Bistite II (BS)	Paste: 001037	Dimethacrylate, MAC-10, Silica-zirconia, Initiator,	Tokuyama Dental, Tokyo, Japan
Linkmax (LM)	A-Paste: 0612052	UDMA, Methacrylated phosphoric acid esters, Silica filler, Fluoro-almino-silicate glass, Initiators, Pigment	GC, Tokyo,Japan
	A-Paste (Catalyst): 0612052	UDMA, Methacrylated phosphoric acid esters, Silica filler, Fluoro-almino-silicate glass, Initiators, Pigment	
RelyX ARC (RX)	Paste: FLGE	Bis-GMA, TEGDMA, , Functionalized DMA, Silane treated ceramic and silica fillers	3M ESPE, St. Paul, MN, USA
Panavia F 2.0 (PF)	A-Paste: 0255AB	Methacrylate, MDP, Quartz-glass, Micorfiller, Photoinitiator	Kuraray Medical, Tokyo, Japan
	B-Paste: 0133AA	Methacrylate, Barium glass, Sodium Fluoride, Chemical initiator	
ResiCem (RC)	Paste: 010701	UDMA, TEGDMA, 2-HEMA, 4-AET, Fluoroaluminosilicateglass, Initiator, Others	Shofu, Kyoto, Japan

MAC-10, 10-methacryloyloxydecamethylene malonic acid; UDMA, urethane dimethacrylate; Bis-GMA, bisphenol A diglycidyl ether dimethacrylate; TEGDMA, triethyleneglycol dimethacrylate; DMA, aliphatic dimethacrylate; MDP, 10-methacryloyloxy-decyl dihydrogenphosphate; HEMA, 2-hydroxyethyl methacrylate; 4-AET, 4-acryloxyethyltrimellitic acid

Stainless steel rods were then bonded to the specimens with each resin cement, and the excess cement was carefully removed with a brush. The bonded specimens were left at room temperature for 30 minutes and then stored in water at 37℃ for 24 hours.

The tensile bond strengths were measured using a universal testing machine (Autograph AGS-J; Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min.

Table 3. Primers used in this study

Material	Batch No.	Composition	Manufacturer
Tokuso Ceramic Primer	003037	Silane coupling agent, Phosphoric acid monomer, alcohol	Tokuyama Dental, Tokyo, Japan
GC Ceramic Primer	A-Primer: 0608072 B-Primer: 0608072	Silane coupling agent, Ethanol UDMA, MMA, Organic acid, Ethanol,	GC, Tokyo,Japan
RelyX Ceramic Primer	6XK	A silane, Ethanol, water	3M ESPE, St. Paul, MN, USA
Clearfil Ceramic Primer	0001BA	3-trimethoxysilylpropyl methacrylate, 10-MDP, Ethanol	Kuraray Medical, Tokyo, Japan
Porcelain Primer (Po)	010701	γ-MPS, Ethanol, Others	Shofu, Kyoto, Japan
AZ Primer (AZ)	010701	6-MHPA, Acetone, Others	Shofu, Kyoto, Japan

UDMA, urethane dimethacrylate; MMA, methyl methacrylate;
MDP, 10-methacryloyloxy-decyl dihydrogenphosphate;
γ-MPS, γ-Methacryloxypropyltrimethoxysilane;
6-MHPA, 6-Methacryloxyhexylphosphonoacetate

After the tensile testing, the fractured interfaces of the specimens were examined with a light microscope (Olympus OCS 912042; Olympus, Tokyo, Japan) at 40× magnification to calculate the debonded area which was assigned to either adhesive (A) or cohesive (C-C) failure modes.

The number of specimens per group was seven. The tensile bond strengths were analyzed by one-way analysis of variance (ANOVA) using the Statistical Package for Medical Science (SPSS Ver.11 for Windows) for statistical procedures to test the effect of the combination of resin cement and primer. Tukey's HSD test was used as post hoc multiple comparisons for the tensile bond strengths to Cercon Base. Since Levene's test indicated significant non-homogeneity among the variances of tensile bond strengths to GN-1 Ceramic Block, Dunnett's T3 test was therefore used as a post hoc multiple comparison. Significance for all the statistical tests was predetermined at a 95% confidential level.

Results

The results of the tensile bond strengths to GN-1 Ceramic Block and Cercon Base are summarized in Table 4. The statistical significance of the bond strengths to GN-1 Ceramic Block and Cercon Base are shown in Tables 5 and 6, respectively. One-way ANOVA revealed that the combination of resin cement and primer had a significant effect on the tensile bond strengths to GN-1 Ceramic Block and Cercon Base, respectively ($p < 0.001$).

Table 4. Tensile bond strength to GN-1 Ceramic Block and Cercon Base

Resin Cement	Treatment	GN-1 Ceramic Block	Cercon Base
BS	(-)	7.7±1.1	9.9±2.0
	(+)	19.5±3.8	14.8±2.1
LM	(-)	15.9±2.8	9.5±1.4
	(+)	23.2±2.4	15.1±3.0
RX	(-)	7.8±1.1	7.1±2.2
	(+)	13.7±2.4	14.0±1.6
PF	(-)	11.5±2.3	10.9±2.5
	(+)	19.5±4.0	19.1±2.9
RC	(-)	7.9±2.2	9.8±1.4
	(+) Po	21.1±2.9	15.6±2.7
	(+) AZ	9.1±1.8	22.3±4.6

n=7, Mean±SD

Table 5. Summary of the statistical analysis of the bond strengths to GN-1 Ceramic Block using ANOVA supplemented with Dunnett's T test

	Cement	BS		LM		RX		PF		RC		
Cement	Treatment	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+, Po)	(+,AZ)
BS	(-)											
	(+)	*										
LM	(-)	*	n.s.									
	(+)	*	n.s.	*								
RX	(-)	n.s.	*	*	*							
	(+)	*	n.s.	n.s.	*	*						
PF	(-)	*	*	n.s.	*	n.s.	n.s.					
	(+)	*	n.s.	n.s.	n.s.	*	n.s.	*				
RC	(-)	n.s.	*	*	*	n.s.	*	n.s.	*			
	(+) Po	*	n.s.	n.s.	n.s.	*	*	*	n.s.	*		
	(+) AZ	n.s.	*	*.	*	n.s.	n.s.	n.s.	*	n.s.	*	

n.s.: no significant differences; *: $p<0.05$

For GN-1 Ceramic Block, the groups with pretreatment showed significantly higher bond strengths than the groups without pretreatment except for RC/(+)AZ. BS/(+), LM/(+), PF(+) and RC/(+Po) provided significantly higher bond strengths than the other groups and there were no significant differences between them. On the other hand, there was no significant difference between RC/(-) and RC/(+)AZ. AZ Primer was not effective for bonding to GN-1 Ceramic Block.

For Cercon Base, there were no significant differences in tensile bond strength in the groups without pretreatment. Conditioning the surface with each primer significantly increased the bond strengths compared to the groups without pretreatment. The combination of ResiCem and AZ Primer showed significantly higher bond strengths than the other groups except for PF/(+). There was no significant difference between RC/(+)AZ and PF/(+).

Table 6. Summary of the statistical analysis of the bond strengths to Cercon Base using ANOVA supplemented with Tukey's HSD T test

	Cement	BS		LM		RX		PF		RC		
Cement	Treatment	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+, Po)	(+, AZ)
BS	(-)											
	(+)	*										
LM	(-)	n.s.	*									
	(+)	*	n.s.	*								
RX	(-)	n.s.	*	n.s.	*							
	(+)	n.s.	n.s.	n.s.	n.s.	*						
PF	(-)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.					
	(+)	*	n.s.	*	n.s.	*	*	*				
RC	(-)	n.s.	*	n.s.	*	n.s.	n.s.	n.s.	*			
	(+) Po	*	n.s.	*	n.s.	*	n.s.	*	n.s.	*		
	(+) AZ	*	*	*	*	*	*	*	n.s.	*	*	

n.s.: no significant differences; *: $p<0.05$

Fracture mode

Tables 7 and 8 show the fracture mode of GN-1 Ceramic Block and CerconBase, respectively. All the fractures after tensile testing occurred either at the interface between the ceramic surface and the cements (adhesive failure) or within the cements (cohesive failure in cements) for both the silica-based ceramics and zirconia-based ceramics.

For GN-1 Ceramic Block, the groups without pretreatment showed completely adhesive failures. BS/(+), LM/(+), PF/(+) and RS/(+)Po showed mainly cohesive failures in the cements, while RX/(+) and RC/(+)AZ showed mostly adhesive failures.

For Cercon Base, the groups without pretreatment showed mainly adhesive failures except for PF/(-). PF/(-) showed mostly cohesive failure in cements. BS/(+),

PF/(+) and RS/(+)AZ showed mostly cohesive failures in cements, while LM/(+) and RX/(+) showed completely adhesive failures.

Table 7. Fracture mode of GN-1 Ceramic Block and Cercon Base. Showing the percentage distributions of adhesive failures (A) and cohesive failures in cements (C-C).

Resin Cement	Treatment	GN-1 Ceramic Block		Cercon Base	
		A	C-C	A	C-C
BS	(-)	100	0	81.42	18.58
	(+)	0	100	4.28	95.72
LM	(-)	100	0	100	0
	(+)	0	100	94.28	5.72
RX	(-)	100	0	100	0
	(+)	95.7	4.3	100	0
PF	(-)	100	0	5.71	94.29
	(+)	0	100	2.85	97.15
RC	(-)	100	0	100	0
	(+) Po	22.86	77.14	85.71	14.29
	(+) AZ	91.43	8.57	2.85	97.15

Discussion

All-ceramic restorations are metal-free alternatives to metal-ceramic composite structures. Over the last few years several all-ceramic systems such as glass-ceramics, glass-infiltrated ceramics, and high-tech ceramics have become established on the market (Anusavice, 1993; Anusavice, 1995; Sorensen, 2000). Their translucency and brightness have made it possible to achieve better esthetic results than with the metal-ceramic restorations.

Tetragonal stabilized zirconia ceramic is the most recently introduced dental all-ceramic material. It exhibits much higher strength and toughness than all the other commercially available dental ceramics (Tinschert *et al.*, 2000; Filser *et al.*, 2001; Kappert and Krah, 2001). It has also become possible to manufacture crowns and multiple-unit dental bridges in zirconia ceramic for *in vitro* testing and clinical use

(Filser *et al.*, 2001; Tinschert *et al.*, 2001). Etching with hydrofluoric acid is not reliable for improving the bond strength of resin cements to zirconia ceramics since their high crystalline content makes them resistant to acid etching (Ozcan and Vallittu, 2003; Derand and Derand, 2000; Yoshida *et al.*, 2004).

The ceramic surfaces were airborne particle abraded in this study. Airborne-particle abrasion with Al_2O_3 is the preferred surface treatment method for high-strength ceramic materials such as alumina and zirconia ceramics (Blatz *et al.*, 2003; Awliya *et al.*, 1998; Kern and Thompson, 1994; Kern and Thompson, 1995; Wegner and Kern M, 2000; Wegner *et al.*, 2002). Airborne-particle abrasion with Al_2O_3 creates high surface energy and promotes micro-retention. Roughening the substrate surface promotes adhesion since it allows the polymer (resin composite) to flow into the surface and forms irregularities on thesubstrate surface (Jennings, 1972).

The bond between silica-based ceramics and resin cements is well-established with application of a silane coupling agent. The use of a silane coupling agent on silica-based ceramics forms a siloxane network with the silica in the ceramic surface, thus improving the ability of resin cements to adhere to the ceramic surface.

For GN-1 Ceramic, treatment with a silane coupling agent was effective for bonding to silica-based ceramics. Failure mode analysis revealed that the groups with silane coupling treatment tended to show cohesive failures in cements, which suggested that the application of the silane coupling agent facilitated chemical bonding between the silica-based ceramics and resin cements (Lu *et al.*, 1992; Della Bona and van Noort, 1995; Debnatha *et al.*, 2003). However, there was no significant difference in the tensile bond strength of ResiCem between with and without AZ Primer pretreatment. The failure mode of the combination of ResiCem and AZ Primer was mainly adhesive failure, suggesting that AZ Primer was not effective for bonding to silica-based ceramics, because of lack of a silane-coupling agent in the primer.

Looking at the data of the tensile bond strengths to zirconia ceramics, no significant differences were found among each resin cement in the groups without pretreatment. Failure mode analysis revealed that the groups without pretreatment

showed mainly adhesive failures except for Panavia F 2.0. When the surfaces of the zirconia ceramics were conditioned with each primer, the tensile bond strengths siginificantly increased compared to the groups without pretreatment. The groups conditioned with primer containing acidic monomers, such as MDP and 6-MHP, showed mostly cohesive failures in the cements, while the groups conditioned with primer containing no acidic monomer showed completely adhesive failures. The improvement in the bond strength using primer pretreatment may have been due to increased wetting of the surface (Wegner and Kern M, 2000; Madani *et al.*, 2000).

It was reported that conventional bonding/silane coupling and resin cements without acidic monomers couldn't provide durable bonds to densely sintered alumina and zirconia ceramics (Kern and Wegner, 1998; Wegner and Kern, 2002: Wegner *et al.*, 2002; Blatz *et al.*, 2003). The acidic monomers in the primer may have been effective in improving adhesion to zirconia ceramics.

Clearfil Ceramic Primer contains MDP. The phosphate ester monomer of MDP was reported to bond directly to metal oxides such as chromium, nickel, aluminum, tin, titanium, and zirconium oxides (Wada, 1986). Previous studies have shown that the application of an MDP-containing bonding/silane coupling agent mixture to zirconium-oxide ceramic restorations yielded superior shear bond strength (Blatz *et al.*, 2004). An MDP-containing resin cement and an MDP-containing bonding/silane coupling agent mixture provided a strong resin bond to airborne-particle-abraded zirconium- and aluminum-oxide ceramic restorations (Kern and Wegner, 1998; Blatz *et al.*, 2003; Blatz *et al.*, 2004).

Pretreatment with AZ Primer showed the highest bond strength of the resin cements to zirconia. AZ Primer contains an acidic monomer, 6-MHPA, but does not contain a silane coupling agent. Ikemura *et al.* (Ikemura *et al.*, 2007) reported that 6-MHPA bonds strongly to metal such as Ni-Cr alloy. The acidic monomers, MDP and 6-MHPA may bond chemically to the zirconium oxide layer coated on the zirconium surface.

In the present study, the early bond strengths of the bonded specimens were tested after 1 day storage in water. However, further studies should be carried out to confirm the durability of the bond of a resin cement to zirconium surface using a pretreatment in vitro. Also, clinical evaluations of zirconia restorations are required to establish reliable application methods.

Conclusions

Within the limitations of this study, the following conclusions were drawn:

(1) Silane coupling treatment significantly increased the bond strengths of resin cements to silica-based ceramics.

(2) Conditioning the zirconia surface with a primer containing acidic monomers was effective in improving the bonding of resin cements to zirconia ceramics.

Chapter 3

Effect of an internal coating technique on tensile bond strengths of resin cements to zirconia ceramics

Introduction

The popularity of all-ceramic restorations has increased in recent years due to their superior esthetic appearance and metal-free structure (Blatz *et al.*, 2003). Computer-aided design and manufacturing (CAD/CAM) has become an increasingly interesting alternative to manual, casting, or pressing techniques.

Zirconia is a high flexural strength ceramic (Piconi C and Maccauro, 1999) which has been used as an orthopedic material (Cales *et al.*, 1994). Based on these improved physical properties compared with alumina-based ceramics, zirconia ceramic was introduced to restorative dentistry for the restoration of posterior teeth. Polycrystalline zirconia is typically used in the tetragonal crystalline phase, stabilized with yttrium oxide (Y-TZP) (Christel *et al.*, 1989 ; Kelly and Denry, 2008). Clinical applications of Y-TZP include all-ceramic cores and post systems (Meyenberg *et al.*, 1995; Lopes *et al.*, 2001) and as copings for complete coverage all-ceramic crowns and fixed partial dentures (McLaren, 1998; Blatz, 2002).

Along with the strength of the material, the cementation technique is also important for the clinical success of a restoration (Burke *et al.*, 2002; Rosenstiel *et al.*, 1998; Umino *et al.*, 2005). Due to their high fracture resistance, zirconium-oxide crowns and FPDs can be cemented using conventional methods recommended by the manufacturers. However, resin bonding between a tooth and the restoration is advocated

for improving the retention, marginal adaptation, fracture resistance of restorations and inhibition of secondary caries (Burke *et al.*, 2002; Rosenstiel *et al.*, 1998; Umino *et al.*, 2005; Jayasooriya *et al.*, 2003).

Obtaining adhesion between resin cement and a ceramic surface requires surface pretreatment (Ozcan and Vallittu, 2003; Ozcan, 2002). The use of a silane coupling agent is recommended for glasses and porcelains in order to form a siloxane network with the silica in the ceramic surface, to improve the bond strength between the resin cement and the ceramic. However, these techniques do not improve the bond strength of zirconium and alumina ceramics because this chemical reaction is not possible with these ceramics. Also, their high crystalline content makes them resistant to hydrofluoric acid etching (Ozcan and Vallittu, 2003; Derand and Derand 2000; Yoshida *et al.*, 2004). For these high strength-ceramics, airborne particle abrasion is an alternative method for roughening the ceramic surface (Kern and Wegner 1998; Ozcan *et al.*, 2001). Blatz *et al.* (Blatz *et al.*, 2004) reported that the use of a MDP-containing bonding/silane coupling agent achieved superior long-term shear bond strength to airborne-particle abraded zirconia ceramic restorations. However, the marginal area of the zirconia frame sometimes chips when air-abraded or adjusted by burs.

Some studies have shown that a tribochemical silica coating increased the bond strength to high-strength ceramics (Kern and Thompson, 1995; Blixt *et al.*, 2000; Blatz *et al.*, 2007). However, it has also been reported that a tribochemical silica coating might be less effective for densely sintered ceramics than for glass-infiltrated ceramics (Amaral *et al.*, 2008). In addition, a tribochemical silica coating cannot cover all the abraded surface with silica.

In order to obtain better bonding to the internal surface of the zirconia-fabricated restoration, we propose a new laboratory technique, the so-called "Internal (INT) Coating Technique". With the INT coating technique, the internal surface of the zirconia restoration is partially or fully covered with a silica-based ceramic by fusion to the zirconia surface. In the laboratory, a zirconia frame with a large marginal or internal gap can be repaired with a silica-based ceramic using the INT coating technique.

Therefore, the purpose of this study was to examine the tensile bond strength of two resin cements to zirconium oxide ceramics pre-treated with or without the INT coating technique compared to that of a silica-based ceramic. The null hypothesis was that INT coating of zirconia ceramics followed by silanization did not increase the bonding of resin cements to zirconia ceramic.

Materials and Methods

Materials used in this study

The ceramic materials used in this study are shown in Table 1. Fifty-six zirconium-oxide ceramic specimens were fabricated from ingots (Cercon Base; Degudent, Hanau, Germany) according to the manufacturer's instructions. The specimens had a diameter of 15 mm and a thickness of 2 mm. Twenty-eight silica-based ceramic specimens (GN-1, GN-1 Ceramic Block; GC, Tokyo, Japan) with a size of 13 × 17 × 21 mm were obtained from the manufacturer. GN-1 was used in order to investigate the effect of silane coupling agents to silica-based ceramics.

The resin cements and the primers for bonding ceramics used in this study are listed in Table 2.

For silanization treatment, a mixture of Clearfil SE Bond Primer and Clearfil Porcelain Bond Activator (Kuraray Medical, Tokyo, Japan) was used for Panavia F 2.0 (PF, Kuraray Medical). Clearfil SE Bond Primer contains an MDP and Clearfil Porcelain Bond Activator contains a silane coupling agent. Porcelain Liner M (Sun Medical, Moriyama, Japan) was used for Superbond C&B (SB, Sun Medical). Porcelain Liner M contains a silane coupling agent and 4-META in MMA.

Table 1. Ceramic materials used in this study

Trade name	Batch No.	Composition	Manufacturer
Cercon Base	18001459	Zirconium dioxide: 89.2wt% Yttrium trioxide: 5.0wt% Hafnium dioxide: < 2.0wt%	Degudent, Hanau, Germany
Cercon Ceram Kiss (Shade: DA3)	34803	Silicon dioxide, Aluminium oxide, Potassium oxide, Lithium oxide, Barium oxide, Boron oxide, Calcium oxide, Cerium oxide, Othrers	Degudent, Hanau, Germany
GN-1 Ceramic Block	0507121	Leucite glass-ceramics	GC, Tokyo, Japan

Table 2-a. Resin cements used in this study

Material	Batch No.	Composition	Manufacturer
Panavia F 2.0 (PF)	A-Paste: 0255AB B-Paste: 0133AA	Methacrylate, MDP, Quartz-glass, Micorfiller, Photoinitiator Methacrylate, Barium glass, Sodium fluoride, Chemical initiator	Kuraray Medical, Tokyo, Japan
Superbond C&B (SB)	Liquid: RR2 Powder: RK1 Catalyst: RR22	MMA, 4-META PMMA Tri-n-butylborane	Sun Medical, Moriyama, Japan

MDP, 10-methacryloyloxy-decyl dihydrogenphosphate; MMA, methyl methacrylate;
4-META, 4-methacryloyloxyethyl trimellitate anhydride; PMMA, polymethyl methacrylate

Table 2-b. Primers used in this study

Material	Batch No.	Composition	Manufacturer
Clearfil Porcelain Bond Activator	00207A	3-trimethoxysilylpropyl methacrylate, Hydrophobic aromatic dimethacrylate and others	Kuraray Medical, Tokyo, Japan
Clearfil SE Bond Primer	00755A	Hydrophilic dimethacrylate, MDP, HEMA, dl-Camphorquinone, N,N-Diethanol-p-toluidine, Water	Kuraray Medical, Tokyo, Japan
Porcelain Liner M	Liquid A: RL1 Liquid B: RL1	MMA, 4-META, Stabilizer MMA, Silane coupling agent, Stabilizer	Sun Medical, Moriyama, Japan

MDP, 10-methacryloyloxy-decyl dihydrogenphosphate; HEMA, 2-hydroxyethyl methacrylate; MMA, methyl methacrylate; 4-META, 4-methacryloyloxyethyl trimellitate anhydride

Table 3. Surface pretreatment protocols applied to each ceramic

Ceramics	abbreviation	surface treatment
Cercon Base	Zr	Polishing with 600 grit-SiC, Air-abrasion with alumina
Cercon Base + Cercon Ceram Kiss	INT	Polishing with 600 grit-SiC, Air-abrasion with alumina, fusing Cercon Ceram Kiss onto the surface of Cercon Base followed by air-abrasion with alumina
GN-1 Ceramic Block	GN-1	Polishing with 600 grit-SiC, Air-abrasion with alumina

Specimen preparation for tensile bond test

The surface pretreatment protocols applied to each ceramic are shown in Table 3. The surfaces of the zirconium-oxide and silica-based ceramic specimens were ground with 600-grit silicon carbide paper using a polishing machine (Ecomet 4; Buehler, Lake Bluff,

IL, USA) and then airborne-particle abraded using a sandblaster (Hi Blaster Ovaljet; Shofu, Kyoto, Japan) with 70- μ m Al_2O_3 particles (Hi Aluminas; Shofu, Kyoto, Japan) at 0.5 MPa air-pressure for 5 seconds at a distance of 10 mm with circular movement in order to air-abrade the circular area approximately 7mm in diameter.

Then, the zirconia specimens were divided into subgroups of 28 each according to the surface pretreatment as follows: no treatment (Zr); and the internal coating technique (INT); the surface of zirconia was coated with micro pearls of fusing porcelain (Cercon Ceram Kiss, dentin shade; Degudent, Hanau, Germany), which is a ceramic veneering material designed exclusively for use with the Cercon Zirconia system. Two stainless steel plates with a thickness of 100 μm were placed on both ends of the zirconia specimen so that the middle of the specimen on which the porcelain would be coated was exposed. Then the porcelain powder was stirred in an excess amount of distilled water and immediately painted on the exposed zirconia ceramic surfaces and then leveled using a spatula in order to standardize the thickness of the porcelain at 100 μm. The stainless steel plates were carefully removed and the porcelain was fired at 820 ℃ for 1 minute in a vacuum to make a coating. After that, the surfaces of INT specimens were air-abraded in the same way as mentioned above.

The specimens were ultrasonically cleaned in distilled water for 10 minutes and air-dried.

A piece of polyethylene tape with a circular hole 4.0 mm in diameter was positioned on the surface of the specimen to demarcate the area of bonding. Following this, the specimens in each group (n=7) were pretreated as follows; no pretreatment as a control (-) or conditioned with silane coupling agent (+).

Stainless steel rods were then bonded to the specimens with each resin cement and any excess was carefully removed with a brush. The bonded specimens were left at room temperature for 30 minutes and then stored in distilled water at 37℃ for 24 hours.

The tensile bond strengths were measured using a universal testing machine (Autograph AGS-J; Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min.

Failure mode analysis

After the tensile test, the fractured interfaces of the specimens were examined with a light microscope (Olympus OCS 912042; Olympus, Tokyo, Japan) at 40 × magnification to examine the debonded area which was assigned to either adhesive failure between ceramics and resin cement (A) or a mixture of adhesive failure and cohesive failure in resin cements (M).

Topographic analysis of the conditioned ceramic surfaces

Ceramic surfaces airborne-particle abraded with 70 μ m Al_2O_3, were examined with a SEM (JSM5310LV; JOEL, Tokyo, Japan) after sputtering using a gold alloy conductive layer of approximately 30 nm.

Surface roughness

In order to measure the surface roughness of the airborne-particle abraded surfaces of each ceramic, four specimens from each group were prepared in the same manner described above. The surface roughness of each specimen was measured with a laser displacement meter (LC-2000; Keyence, Osaka, Japan) and was expressed as the average roughness (Ra) value as was used previously (Daneshmehr *et al.*, 2008)

Statistical analysis

The number of specimens per group was seven. The tensile bond strengths were initially analyzed by three-way analysis of variance (ANOVA) to examine the effects of resin cement, ceramic substrate, and silanization. However, as there were significant interactions between all three factors, the data were analyzed by two-way ANOVA using the Bonferroni test to examine the effects of ceramic substrate, silanization, and the interaction between these two factors. The data for Ra values were analyzed by one-way ANOVA using the Dunnett's T3 test. Significance for the above statistical tests was predetermined at a 95% confidence level, whilst the failure mode distributions were analyzed by chi-square test to a 99% confidence level.

Results

Tensile bond strength

The results of the tensile bond strengths of PF and SB to each ceramic are summarized in Table 4 and 5, respectively. Statistically significant differences between resin cement, ceramic substrate, and silanization are indicated in the same Tables. Two-way ANOVAs revealed that the bond strengths of PF were influenced by both ceramic substrate ($F=4.502$, $p=0.018$) and silanization ($F=427.533$, $p<0.001$), and there was a significant interaction between the independent variables, ceramic substrate and silanization ($F=18.381$, $p<0.001$). It was also revealed that the bond strengths of SB were influenced by both ceramic substrate ($F=6.642$, $p=0.004$) and silanization ($F=89.229$, $p<0.001$), and there was a significant interaction between the independent variables, ceramic substrate and silanization ($F=31.137$, $p<0.001$).

Table 4. Tensile bond strength of Panavia F 2.0 to Zr, INT and GN-1 (MPa)

Silane coupling treatment	Zr	INT	GN-1
-	$7.5^{A,a}$ (1.5)	$4.9^{A,c}$ (0.9)	$5.8^{A,e}$ (0.5)
+	$10.7^{B,b}$ (1.2)	$14.5^{C,d}$ (1.1)	$13.0^{C,f}$ (1.2)

n=7. All values are mean (SD). Within the same row, means with the same large superscript letter are not statistically different ($p<0.05$). Within the same column, means with the same small superscript letter are not statistically different ($p<0.05$).

Table 5. Tensile bond strength of Superbond C&B to Zr, INT and GN-1 (MPa)

Silane coupling treatment	Zr	INT	GN-1
-	$12.0^{A,a}$ (1.7)	$9.7^{B,b}$ (1.4)	$12.4^{A,d}$ (1.4)
+	$12.7^{C,a}$ (1.5)	$18.9^{D,c}$ (1.4)	$15.5^{E,e}$ (1.4)

n=7. All values are mean (SD). Within the same row, means with the same large superscript letter are not statistically different ($p<0.05$). Within the same column, means with the same small superscript letter are not statistically different ($p<0.05$).

For PF, the groups with silanization significantly improved the tensile bond strengths compared to the groups without silanization in each ceramic. INT/(+) showed significantly higher tensile bond strength than Zr/(+). On the other hand, there was no significant difference between INT/(+) and GN-1/(+).

For SB, silanization significantly improved the bond strength compared to the groups without silanization in INT and GN-1, however, silanization was not effective for Zr. INT/(+) showed significantly higher bond strength than Zr/(+) and GN-1(+).

Failure mode analysis

The failure mode distributions are summarized in Table 5. None of the fracture occurred at the interface of the stainless steel rods. All the fractures after tensile testing occurred in 2 locations as follows: adhesive failure between the ceramic and the cement; and mixed failure involving adhesive failure and cohesive failure within the cement for both the silica-based ceramics and zirconia-based ceramics. Chi-square test indicated that there were no significant differences in failure mode between resin cement, ceramic substrate and silanization ($p>0.01$).

Table 6. The failure mode distributins.

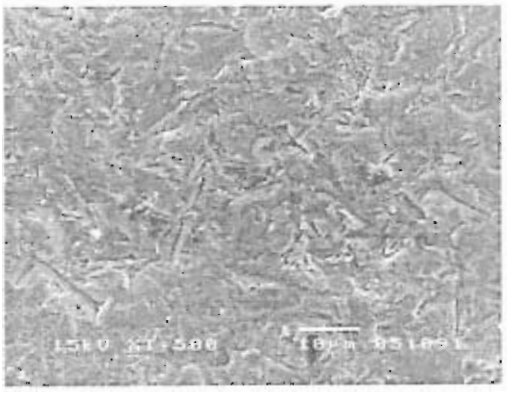
Ceramic	Resin cement	Silane	A	M
Zr	PF	(-)	4	3
		(+)	0	7
	SB	(-)	0	7
		(+)	0	7
INT	PF	(-)	4	3
		(+)	2	5
	SB	(-)	2	5
		(+)	0	7
GN-1	PF	(-)	3	4
		(+)	0	7
	SB	(-)	2	5
		(+)	0	7

A: Adhesive failure between the ceramic surface and the cement; M: Mix Failure involving adhesive failure and cohesive failure in the cement

Topographic analysis of the conditioned ceramic surfaces

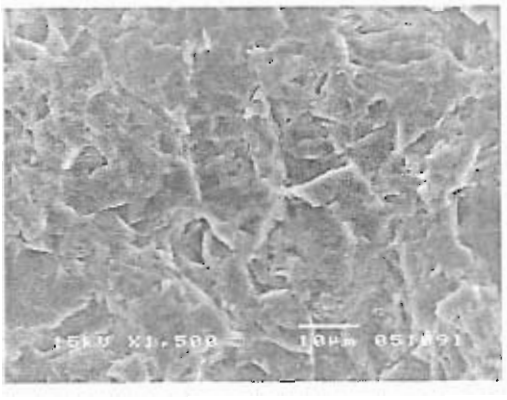
Figure 1 shows the SEM images of the ceramic surfaces after airborne-particle abrasion. Airborne-particle abrasion with Al_2O_3 altered the superficial ceramic layer and created sharp edges and grooves. Zr (Fig 1-a) exhibited a surface with small irregularities whereas INT (Fig 1-b) and GN-1 (Fig 1-c) showed similar surfaces with large irregularities.

Figure 1. SEM photographs of the ceramic surfaces airborne-particle abraded with 50μm Al_2O_3. (×2000)
Zr (a) showed surface with small irregularities whereas INT (b) and GN-1 (c) showed similar surfaces with large irregularities.



(a) Zr

(b) INT



(C) GN-1.

Surface roughness

Means and standard diviations of the surface roughness (Ra) for each ceramic airborne-particle abraded with 70 μm Al_2O_3 are shown in Table 7. The surface roughness of INT and GN-1 was significantly higher than that of Zr ($p<0.05$), whereas there was no difference between INT and GN-1 ($p>0.05$).

Table 7. Surface roughness values (Ra) of each ceramic airborne-particle abraded with 70μm Al_2O_3.

Ceramics	Surface roughness (μm)
Zr	5.4^{A} (0.5)
INT	21.3^{B} (3.6)
GN-1	17.9^{B} (5.4)

Means with the same large superscript letter are not statistically different ($p<0.05$).
n=4. All values are mean (SD).

Discussion

Tetragonal stabilized zirconia ceramic is the most recently introduced dental all-ceramic material. It exhibits much higher strength and toughness than all the other commercially available dental ceramics (Tinschert *et al.*, 2000; Filser *et al.*, 2001).

The bond between silica-based ceramics and resin cements is well-established with the application of a silane coupling agent. The use of a silane coupling agent on silica-based ceramics forms a siloxane network with the silica in the ceramic surface. However, establishing a strong and stable bond with zirconia has proven to be difficult, as the material is acid resistant and does not respond to common etching and silanization procedures (Blatz et al., 2003).

Airborne-particle abrasion with Al_2O_3 is the preferred surface treatment method for high-strength ceramic materials, such as alumina and zirconia ceramics (Blatz *et al.*, 2003; Kern and Thompson, 1994; Kern and Thompson, 1995; Awliya *et al.*, 1998, Wegner and Kern, 2000; Wegner *et al.*, 2002), which creates high surface energy and

promotes micro-retention. However, the results of the surface roughness and SEM images showed the air-abraded surfaces of Zr to have smaller irregularities compared to those of GN-1 and INT. Airborne particle abrasion increased the mean flexural strength and the monoclinic phase of TZP (Guazzato *et al.*, 2005; Kosmac *et al.*, 1999). Some manufacturers recommend heat treatment for zirconia after airborne particle abrasion in order to cause the reverse monoclinic (*m*)→ tetragonal (*t*) phase transformation. However, heat treatment was not applied according to the manufacturer's instructions in this study.

Previous studies have reported that tribochemical silica coating on zirconia ceramics improved bonding to the zirconia surface (Kern and Thompson, 1995; Blixt *et al.*, 2000; Blatz *et al.*, 2007). In this technique, the surfaces are air-abraded with silica-coated alumina particles (Kern and Thompson, 1995; Blixt *et al.*, 2000). The blasting pressure results in the embedding of silica particles on the ceramic surface, rendering the silica-modified surface chemically more reactive to the resin through silane coupling agents. However, de Oyagüe *et al.* (de Oyagüe *et al.*, 2008) has recently reported that tribochemical silica coating followed by silanization was not effective for zirconia with a phosphate monomer-containg cement nor a conventional Bis-GMA resin cement.

In the present study, the bond strengths of PF and SB to INT were significantly higher than those to Zr after 24 hours water storage. For the INT coating groups, silanization significantly increased the tensile bond strengths in both PF and SB. This indicates that a chemical bond resulting from the formation of a siloxane network was facilitated between the resin cement and the surface of the INT coating. In addition, it was reported that the silane coupling agents improve the wettability of ceramic surface (Ozcan, 2003). The INT coating technique followed by silanization showed equivalent bond strengths to GN-1. In the INT coating group, there were no adhesive failures at the interface between zirconia and veneering porcelain, nor cohesive failures in veneering porcelain, which indicates that the bonding of veneering porcelain to zirconia exceeded that of resin cements to veneering porcelain. Previous studies (Fischer *et al.*, 2008; Aboushelib *et al.*, 2005) have reported that the bond strength between zirconia and

veneering porcelain ranged between 23 MPa and 33 MPa, depending on the material, test method and surface treatment of zirconia. In the present study, the failure modes didn't always correspond to that of tensile bond strengths. This might have been related to the difference in the mechanical properties of the substrates among Zr, INT and GN-1 and also the two resin cements.

The tensile bond strength of PF was lower than that of SB in each group. PF is a dual-cured resin cement. The resin cement was polymerized without additional light as it is questionable if the light can reach to cements through zirconia frame in clinical situations. Therefore, PF may not have been polymerized in the best condition, which might explain the lower tensile bond strength of PF compared to that of SB. SB is a MMA-based resin cement. The elastic modulus of MMA-based cement is lower than that of dimethacrylate-based cement (Kitasako *et al.*, 1995). Kitasako *et al.* (Kitasako *et al.*, 1995) suggested that the shear bond strengths of resin cements may be influenced by their material properties. The monomer of SB might have penetrated the air-abraded zirconia surafce more easily than that of PF because of the smaller molecular size of MMA (Nakabayashi *et al.*, 1982).

For the Zr groups, applying a mixture of Clearfil SE Bond Primer and Clearfil Porcelain Bond Activator significantly increased the tensile bond strength in PF. Clearfil SE Bond Primer contains a phosphate ester monomer of MDP, which has been demonstrated to bond directly to metal oxides (Wada, 1986). Previous studies have shown that the application of an MDP-containing bonding/silane coupling agent mixture to zirconium-oxide ceramic restorations yielded superior shear bond strength(Kern and Wegner, 1998; Blatz *et al.*, 2003; Blatz *et al.*, 2004).

Porcelain Liner M contains a carboxylic acid monomer, 4-META, which is supposed to have a chemical affinity to metal oxides (Ohno *et al.*, 2004; Hummel and Kern, 2004). However, the present study showed that the application of Porcelain Liner M did not improve the bond strength. Ozcan *et al.* (Ozcan *et al.*, 2008) reported that all the zirconia specimens bonded with Superbond debonded after thermal cycling. On the contrary, Derand *et al.* (Derand and Derand, 2000) reported that the bond strength of Superbond to zirconia did not decrease after 2 months water storage compared to that

after one day.

Reuter *et al.* (Reisch *et al.*, 2005) reported that silanized interfaces appear to be unstable in humid conditions and the silane bond was found to deteriorate in moisture. Since the resins are permeable to water, the bond between silane and resin composite was expected to deteriorate by hydrolysis over time.

Beuer *et al.* (Beuer *et al.*, in press) reported that three CAD/CAM systems of zirconia fabrication showed marginal gaps below 120 μm which were considered clinically acceptable. On the other hand, Reisch *et al.* (Reisch *et al.*, 2005) reported that the marginal gaps and internal fitness of zirconia fabricated FPDs varied between 8 μm and 272 μm, and between 39 μm and 502 μm, respectively. In clinical situations, the coating should be thin when the gap is small. On the other hand, after sintering or adjusting by burs, a zirconia frame with a large marginal or internal gap can be repaired fully or partially with a silica-based ceramic using the INT coating in the laboratory. The porcelain coating of 100 μm was made experimentally to standardize the thickness by a dental technician in the present study. We are currently investigating the internal fitness and the marginal adaptation of the zirconia frame using the INT coating with different thickness and techniques.

Therefore, further studies should be carried out to confirm the hydrolytic stability of the bond of resin cement to a zirconium surface using the INT coating technique in vitro, and also the application of the INT coating technique in the laboratory should be improved. Moreover, clinical evaluations of zirconia restorations are required to establish reliable application methods.

Conclusions

Within the limitations of this study, the following conclusions were drawn: Surface treatment of zirconia using the INT coating technique followed by silanization can successfully increase the bond strength of the resin cements to zirconia ceramics.

CHAPTER 4

The effects of an internal coating technique and silane coupling agents on tensile bond strengths of a resin cement to zirconia ceramics.

Introduction

Since zirconia is tough, has high strength, is a metal-free material, and its color is sufficiently white, it is used today in many dental ceramic systems (van Noort, 2002), and also in biomedical applications (Piconi and Maccauro, 1999).

Due to their high resistance to fracture, complete-coverage zirconium oxide–based crowns can be cemented conventionally, as recommended by some manufacturers (Ernst, 2005). However, the cementation technique is important for the clinical success of a restoration (Burke *et al.*, 2000; Rosenstiel *et al.*, 1998; Umino *et al.*, 2005). Bonding between the tooth substrate and the restoration is advocated for improving the retention, marginal adaptation and inhibition of secondary caries (Burke *et al.*, 2000; Rosenstiel *et al.*, 1998; Umino *et al.*, 2005; Jayasooriya *et al.*, 2003).

Acid etching and silanization are not expected to improve adhesion of resin cement to high-strength ceramics, such as alumina and zirconia-based materials, because they have little or no silica content (Awliya *et al.*, 1998; Blixt *et al.*, 2000; Kern and Thompson, 1995; Madani *et al.*, 2000; Ozcan *et al.*, 2001; Wegner and Kern, 2000) . For zirconia ceramics, airborne particle abrasion is an alternative method for roughening the ceramic surface (Wegner and Kern, 2000; Kern and Wegner, 1998; Blatz *et al.*, 2003). Blatz *et al.* (Blatz *et al.*, 2004) reported that the use of a MDP-containing bonding/silane coupling agent achieved superior long-term shear bond strength to

airborne-particle abraded zirconia ceramic restorations.

In order to obtain better bonding to the internal surface of the zirconia-fabricated crown, we propose a new laboratory technique, the so-called "Internal (INT) Coating Technique". With the INT coating technique, the internal surface of the zirconia restoration is fully or partially covered with a silica-based ceramic by fusion to the surface.

Therefore, the purpose of this study was to examine the effect of the INT coating technique and silane coupling agents on the tensile bond strength of a resin cement to zirconium oxide ceramics. The null hypothesis is that there are no differences in the adhesion of resin cement to zirconia whether the INT coating is used or not and whether different silane coupling agents are used.

Materials and Methods

Materials used in this study

The ceramic materials used in this study are shown in Table 1. Sixty-four zirconium-oxide ceramic specimens were fabricated from ingots (Cercon Base; Degudent, Hanau, Germany) according to the manufacturer's instructions. The specimens had a diameter of 15 mm and a thickness of 2 mm.

The resin cements and primers used in this study are shown in Table 2. Panavia F 2.0 (PF, Kuraray Medical, Tokyo, Japan) is a dual-cured resin cement which contains an acidic monomer 10-methacryloyloxy-decyl dihydrogenphosphate (MDP).

For silanization, one of two silane coupling agents; a mixture of Clearfil SE Bond Primer and Clearfil Porcelain Bond Activator (SEP/PBA), and Clearfil Ceramic Primer (CP) were used. SEP contains an MDP whereas PBA contains a silane coupling agent, 3-trimethoxysilylpropyl methacrylate. Clearfil Ceramic Primer is a new single-component adhesive primer which contains both 3-trimethoxysilylpropyl methacrylate and MDP.

Table 1. Ceramic materials used in this study

Trade name	Batch No.	Composition	Manufacturer
Cercon Base	18001459	Zirconium dioxide: 89.2wt% Yttrium trioxide: 5.0wt% Hafnium dioxide: < 2.0wt%	Degudent, Hanau, Germany
Vintage ZR (shade: B4B)	070704	Silicon dioxide, Aluminium oxide, Potassium oxide, Sodium oxide, Calcium oxide, Boron trioxide, Pigment, Fluorescence	Shofu, Kyoto, Japan

Table 2. Resin cements and primers used in this study

Material	Abbreviation	Batch No.	Composition
Panavia F 2.0	PF	A-Paste: 0255AB	Methacrylate, MDP, Quartz-glass, Micorfiller, Photoinitiator
	SEP	B-Paste: 0133AA	Methacrylate, Barium glass, Sodium fluoride, Chemical initiator
Clearfil SE Bond Primer		00755A	Hydrophilic dimethacrylate, MDP, HEMA, dl-Camphorquinone, N,N-Diethanol-p-toluidine, Water
Clearfil Porcelain Bond Activator	PBA	00207A	3-trimethoxysilylpropyl methacrylate, Hydrophobic aromatic dimethacrylate and others
Clearfil Ceramic Primer	CP	0001BA	3-trimethoxysilylpropyl methacrylate, MDP, Ethanol

MDP, 10-methacryloyloxy-decyl dihydrogenphosphate;
HEMA, 2-hydroxyethyl methacrylate
Manufacturer: Kuraray Medical, Tokyo, Japan

Specimen preparation for tensile bond test

The surfaces of the zirconia specimens were ground with 600-grit silicon carbide paper

using a polishing machine (Ecomet 4; Buehler, Lake Bluff, IL, USA), and then airborne-particle abraded using a sandblaster (Hi Blaster Ovaljet; Shofu, Kyoto, Japan) with 70 μm Al_2O_3 particles (Hi Aluminas; Shofu; Kyoto, Japan) at 0.3 MPa air-pressure for 5 seconds at a distance of 10 mm from the surface.

Then, they were divided into two subgroups of 32 each, according to the surface pretreatment as follows: no pretreatment (Zr); and pretreatment of the internal coating technique (INT). For the INT coating group, the surface of zirconia was coated with a medium fusing porcelain (Vintage ZR, shade B4B; Shofu, Kyoto, Japan), which is a ceramic veneering material designed exclusively for use with the zirconia framework. The porcelain powder was stirred in an excessive amount of water and immediately painted on the ceramic surfaces and fired at 925 ℃ for 1 minute with vacuum to make a coating with a thickness of 200 μm. The surface of the INT coating was airborne-particle abraded in the same way as mentioned above.

Then, the specimens of Zr and INT were ultrasonically cleaned in distilled water for 10 minutes and air-dried. A piece of polyethylene tape with a circular hole of 4.0 mm in diameter was positioned on the surface of the specimen to demarcate the area of bonding. Following this, the specimens in each group (n=8) were conditioned with either SEP/PBA or CP according to the manufacturer's instructions.

Stainless steel rods were then bonded to the specimens with PF, and the excess cement was carefully removed with a brush. The bonded specimens were left at room temperature for 30 minutes before chemically setting of the resin cement. Prior to testing, all bonded specimens were stored in water at 37 ℃ for 24 hours and half of them were additionally subjected to thermal cycling (TC) of 5000 times in water (5-55 ℃, dwell time of 30 seconds each).

The tensile bond strengths were measured using a universal testing machine (Autograph AGS-J; Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min.

Failure mode analysis

After the tensile testing, the fractured interfaces of the specimens were examined with a

light microscope (Olympus OCS 912042; Olympus, Tokyo, Japan) at 40 × magnification to examine the debonded area. Modes of failure were classified as follows: more than 80 % adhesive failure between ceramic and resin cement and less than 20 % cohesive failure in the resin cement (mode 1), or less than 80 % adhesive failure between ceramic and resin cement and more than 20 % cohesive failure in the resin cement (mode 2).

Topographic analysis of the conditioned ceramic surfaces

Ceramic surfaces airborne-particle abraded with 70 μm Al_2O_3 were examined with a scanning electron microscope (SEM) (JSM5310LV; JOEL, Tokyo, Japan) after sputtering using a gold alloy conductive layer of approximately 30 nm.

Statistical analysis

The number of specimens per group was eight. The tensile bond strengths were initially analyzed by three-way analysis of variance (ANOVA) to examine the effects of ceramic substrate, silane coupling agent and thermal cycling. Moreover, as there were no significant interactions between all three factors, two separate two-way ANOVAs; one for the bond strengths with SEP/PBA and one for the bond strengths with CP, were completed to examine the effects of ceramic substrate, thermal cycling, and the interaction between these two factors, respectively.

Significance for the above statistical tests was predetermined at a 95% confidence level, whilst the failure mode distributions were analyzed by chi-square test to a 99% confidence level.

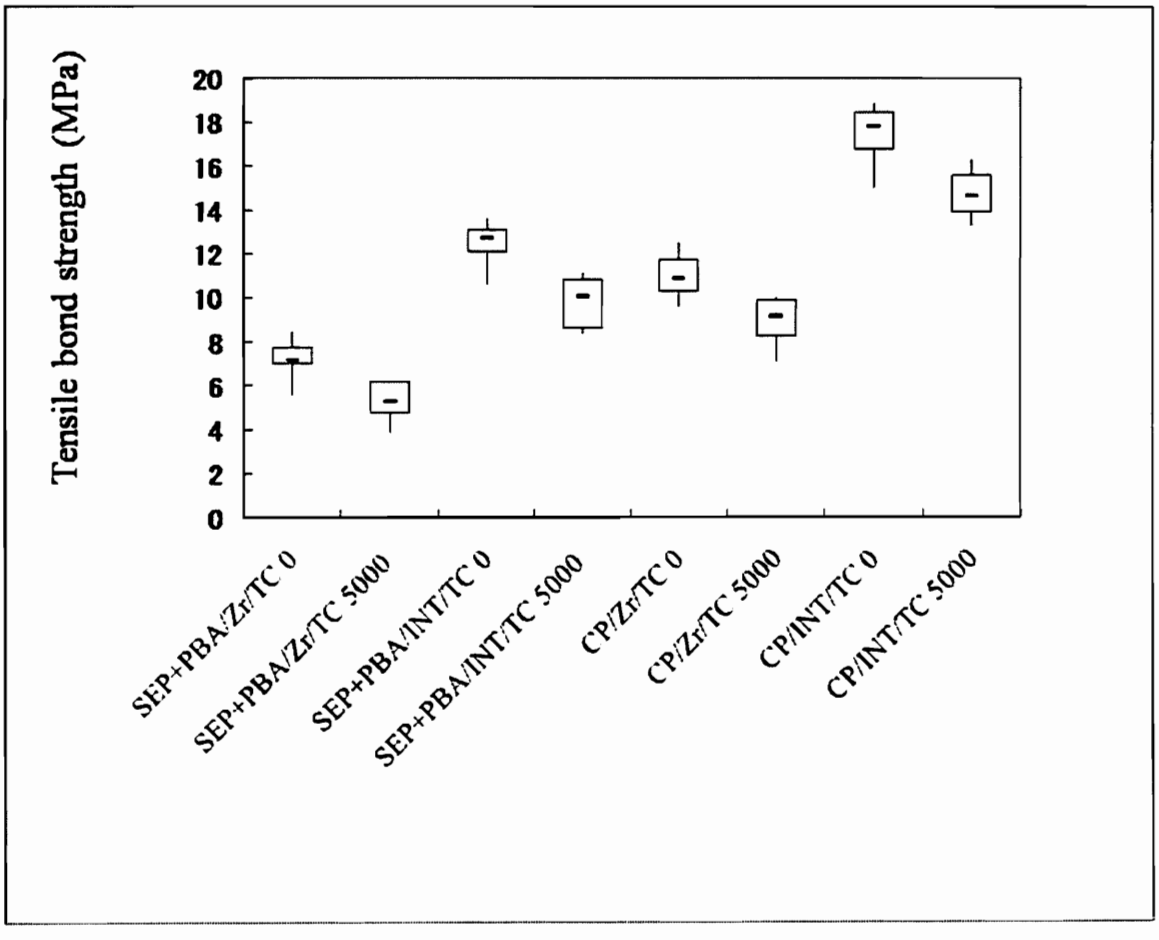
Results

Tensile bond strength

Figure 1 and Table 3 summarizes the bond strengths of PF with either CP or SEP/PBA to Zr and INT before and after TC. According to two-way ANOVAs (Table 4), bond strength was significantly influenced by both ceramic substrate and thermal cycling, however, the interaction between ceramic substrate and thermal cycling was not

significant, for both SEP/PBA and CP.

Figure 1. Box plot of the tensile bond strength of PF with SEP/PBA or CP to Zr and INT before and after thermal cycling. The box represents the spreading of the data between the first and third quartile. The bur (-) inside the box represents the median. The whiskers extend to the minimum and maximum values measured. TC 0: no thermal cycling; TC 5000: 5000 cycles of thermal cycling



Therefore, the INT coating technique significantly increased the bond strengths compared to Zr independent of silane coupling agent and thermal cycling ($p<0.001$). However, thermal cycling significantly decreased the bond strengths independent of ceramic substrate and silane coupling agent ($p<0.001$). The application of CP yielded significantly higher bond strengths than SEP/PBA independent of ceramic substrate and thermal cycling ($p<0.001$).

Table 3. Tensile bond strength of PF with either SEP/PBA or CP to Zr and INT before and after TC (MPa)

Silane coupling agent	Ceramic substrate	TC 0	TC 5000
SEP/PBA	Zr	7.12±1.03	5.28±0.95
	INT	12.48±0.95	9.85±1.14
CP	Zr	10.98±1.01	8.97±1.08
	INT	17.45±1.44	14.78±1.13

n=8. Mean±SD.

Table 4. Analysis of variance results for tensile bond strength

Source	DF	SS	MS	F	P
(a) ANOVA for SEP/PBA					
Ceramic substrate	1	302.21	302.21	218.47	0.000
Thermal cycling	1	43.77	43.77	31.64	0.000
Ceramic substrate* Thermal cycling	1	0.87	0.87	0.62	0.435
Error	28	38.73	1.38		
Total	32	5829.82			
(b) ANOVA for CP					
Ceramic substrate	1	195.16	195.16	187.94	0.000
Thermal cycling	1	40.69	40.69	39.19	0.000
Ceramic substrate* Thermal cycling	1	1.12	1.12	1.08	0.308
Error	28	29.08	1.04		
Total	32	2638.20			

Failure mode analysis

The failure mode distributions are summarized in Table 5. None of the fracture occurred at the interface between the resin cement and the stainless steel rods. The results of the chi-squared comparisons revealed no significant difference in the failure mode among the eight groups presented in Table 5 ($p>0.01$).

Table 5. The failure mode distributions.

Ceramic substrate	Silane coupling agent	Thermal cycling	Mode 1	Mode 2
Zr	SEP/PBA	0	5	3
		5000	6	2
	CP	0	5	3
		5000	3	5
INT	SEP/PBA	0	5	3
		5000	3	5
	CP	0	2	6
		5000	2	6

Mode 1: More than 80 % adhesive failure between ceramic and resin cement and less than 20 % cohesive failure in the resin cement; Mode 2: Less than 80 % adhesive failure between ceramic and resin cement and more than 20 % cohesive failure in the resin cement.

Topographic analysis of the conditioned ceramic surfaces

Figure 2 shows the SEM images of the ceramic surfaces after airborne-particle abrasion. Airborne-particle abrasion with Al_2O_3 altered the superficial ceramic layer and created sharp edges and grooves for both Zr (Figure 2-a) and INT (Figure 2-b).

Figure 2. The SEM images of the ceramic surfaces airborne-particle abraded with 50-μm Al_2O_3 (×1500). The surfaces of both Zr (a) and INT (b) were roughend.

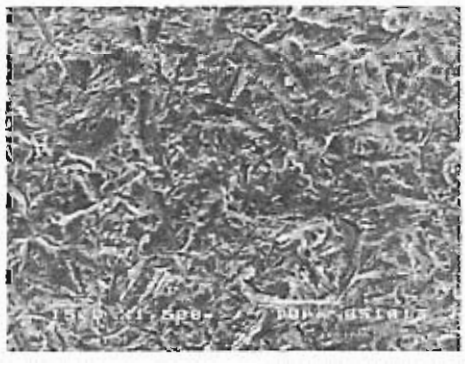


Figure 2-a. Zr

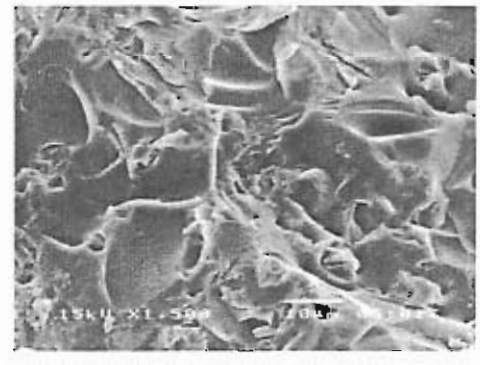


Figure 2-b. INT

Discussion

The ceramic surface was air-abraded with alumina particles in this study. Airborne-particle abrasion with alumina particles is believed to be the preferred surface treatment method for high-strength ceramic materials, such as alumina and zirconia ceramics which creates high surface energy and promotes micro-retention (Blatz *et al.*, 2003; Kern and Thompson, 1994; Kern and Thompson, 1995; Awliya *et al.*, 1998, Wegner and Kern, 2000; Wegner *et al.*, 2002). Roughening the substrate surface promotes adhesion, since it allows the polymer (resin composite) to flow into the surface and forms irregularities on the substrate surface (Jennings, 1972).

Previous studies have reported that a tribochemical silica coating on zirconia ceramics improved bonding to alumina and zirconia surface (Blixt *et al.*, 2000; Kern and Thompson, 1995; Blatz *et al.*, 2007). In tribochemical silica coating, the surface of the restoration is air-abraded with the silica-coated alumina particles (Blixt *et al.*, 2000; Kern and Thompson, 1995). The blasting pressure results in embedding of silica particles on the ceramic surface, rendering the silica-modified surface chemically more reactive to resin through a silane coupling agent. Conversely, de Oyagüe *et al.* (de Oyagüe et al., in press) has reported that tribochemical silica coating followed by silanization was not effective for zirconia with a phosphate monomer-containg cement nor a conventional Bis-GMA resin cement.

The INT coating is considered to be more effective treatment than the tribochemical silica coating in covering the zirconia surface with silica. The surfaces of zirconia were treated by fusing a silica-baesd veneering ceramics for the zirconia framework. The heat expansion coefficient of the veneering ceramics is designed close to that of zirconia ceramics.

A dual-cured resin cement, Panavia F 2.0, was polymerized without additional light irradiation in this study in order to simulate the severe clinical situation. It is questionable if the light can reach to cements through zirconia frame, because of the optical opacity of zirconia.

Two commercially available silane coupling agents; SEP/PBA and CP were

used in this study, both of which contain a phosphate ester monomer of MDP, which is also contained in PF. It was reported that MDP bonded directly to metal oxides such as chromium, nickel, aluminium, tin, titanium, and zirconium oxides (Wada, 1986). Applying a mixture of an MDP-containing bonding agent/silane coupling agent yielded a superior and durable shear bond strength to zirconium-oxide ceramic restorations abraded with alumina particles (Blatz *et al.*, 2004). Moreover, an MDP-containing resin cement with an MDP-containing bonding/silane coupling agent provided a strong bond to airborne-particle abraded zirconium- and aluminium- oxide ceramic restorations (Ozcan *et al.*, 2001; Blatz *et al.*, 2003; Blatz *et al.*, 2004).

The INT coating enhanced the bond strength to zirconia in the presence of an MDP/silane coupling agent-containing primer. The increase of the bond strength with the INT coating may be due to chemical bonding by forming a siloxane network successfully. In the INT coating group, there was no adhesive failure at the interface between the zirconia surface and the fused porcelain, nor cohesive failures in the fused porcelain. That means the bonding of the fused porcelain to the zirconia surface exceeded the tensile force up to failure.

Thermal cycling was carried out to investigate the bonding durability of the resin cement to zirconia in this study. For the Zr groups, thermal cycling significantly reduced the tensile bond strengths regardless of silane coupling agents used. Reactions might have formed between the hydroxyl groups in MDP monomer and the hydroxyl groups on zirconia ceramic surface, but these chemical reactions did not maintain their strength after thermal cycling. Valandro *et al.* (Valandro *et al.*, 2007) also reported inferior Panavia-zirconia adhesion results, with a significant reduction after 12,000 thermal cycles and/or 300 days of long-term water storage. For the INT groups, thermal cycling also significantly reduced the tensile bond strengths regardless of silane coupling agents used. Water storage and thermal cycling were described as detrimental to the silane-ceramic bond (Ozcan *et al.*, 1998). In addition, the used auto-curing mode of a dual cured resin cement might be responsible for the unstable bond strength after thermal cycling for both Zr and INT groups as the polymerization of PF might have been insufficient.

The failure modes didn't always correspond to that of tensile bond strength results in this study. This might be related to a difference in the mechanical properties of the substrates between Zr and INT. Moreover, the used auto-curing mode may have resulted in the lower mechanical property of the cement, leading to cohesive failures at low bond strengths in some specimens.

CP demonstrated significantly higher bond strengths than SEP/PBA independent of ceramic substrate and thermal cycling. Although both CP and SEP/PBA contain the same phosphoric acid monomer (MDP) and silane coupling agent (3-trimethoxysilylpropyl methacrylate), this result might be attributed to differences between the two materials in terms of monomer composition, initiator, and solvent. It can be assumed that CP is a single-bottle adhesive primer containing proper combination of MDP and 3-trimethoxysilylpropyl methacrylate for pretreatment of ceramics.

For the INT coating, the 200 μm thick silica-based ceramics was fused on the zirconia surface by a dental technician. The INT coating is designed as a laboratory technique to enhance the bonding between zirconia and resin cement and also improve internal adaptation by fusing a silica-based ceramics to the internal surface of the zirconia restoration. Reisch *et al.* (Reisch *et al.*, 2005) reported that the marginal gaps and internal fitness of zirconia fabricated fixed partial dentures (Lava) varied between 8 μm and 272 μm, and between 39 μm and 502 μm, respectively. We speculate that the zirconia restorations with poor marginal or internal fitness can be repaired partially or fully using the INT coating in the laboratory before cementation.

It must be considered that *in vitro* testing is more simplified than the *in vivo* situation. In this study, thermal cycling was used as means of aging, however, teeth in the oral environment are continuously subjected to different types of stresses that may impair the bonding effectiveness of the cement. Therefore, further studies should be carried out to evaluate the long-term durability. Moreover, clinical evaluations of zirconia restorations are also required to establish reliable application methods.

Conclusions

The results of this study suggested that the INT coating technique with a silane coupling agent could improve the bonding of a dual-cured resin cement to zirconia. However, the bond strength significantly reduced after thermal cycling.

Chapter 5

Effect of resin coating on adhesion and microleakage of CAD/CAM fabricated all-ceramic crowns after occlusal loading *in vitro*

Introduction

All-ceramic crowns are characterized by enhanced esthetic properties, optimal integration to gingival tissues, and biocompatibility (Fradeani and Redemagni, 2002) (Oden *et al.*, 1998). These restorations can be fabricated with a variety of systems, including the CEREC CAD-CAM system (Sirona Dental Systems GmbH, Bensheim, Germany), which offers the dentist the opportunity to prepare, design and fabricate a ceramic restoration in a single appointment, without the need for making impressions, provisional restorations or dental laboratory support (Mormann *et al.*, 1987).

The strength of all-ceramic crowns is influenced by the form of the tooth preparation, pretreatment of the crown and abutment, and the method of luting (Burke, 1995). The adhesive luting technique, including dentin bonding agent and dual-curing resin cement, is now recommended for the luting of many all-ceramic systems (Pospiech, 2002). On the ceramic side, the bond is usually produced via two mechanisms, by micro-mechanical interlocking following hydrofluoric acid etching and/or air-abrasion, as well as by chemical bonding using a silane coupling agent (Stangel *et al.*, 1987; Roulet *et al.*, 1995). It has been shown that all-ceramic restorations cemented with adhesive materials have superior fracture resistance compared with those cemented with conventional cements (Casson *et al.*, 2001).

Despite all these technological advances, obtaining an effective and

long-lasting marginal seal at the tooth-restorative material interface is still a great challenge. The clinical performance of the dentin bond is impaired by composite polymerization shrinkage and stresses due to thermal dimensional changes (Van Meerbeek *et al.*, 1998). Therefore, the strength of the dentin bonding agents to resist the polymerization shrinkage of resin cements on the dentin surface is of great importance for the prevention of microleakage. Microleakage of crowns is considered to be one of the main causes of failure and one of the factors that most influences the clinical longevity of indirect restorations (Tay *et al.*, 2002).

Although resin bonding between a tooth and the restoration is advocated for improving the retention, marginal adaptation, fracture resistance of restorations and inhibition of secondary caries (Burke *et al.*, 2002; Rosenstiel *et al.*, 1998; Umino *et al,*. 2005), current resin cements do not always provide reliable bonding to dentin compared with dentin bonding systems for direct resin composite restorations (Burrow *et al.*, 1996). A relatively weak bond of a resin cement may lead to poor adaptation and gap formation around the composite restoration (Piwowarczyk *et al.*, 2005), postoperative sensitivity (Christensen, 2000) and reduced longevity of the restoration (Burrow *et al.*, 1996). Catastrophic fracture has been the most frequently reported reason for failure of all-ceramic restorations (Sjogren *et al.*, 2004; Kramer *et al.*, 2006). It has been demonstrated through retrieval studies of failed glass-ceramic crowns that the majority of fractures tend to initiate from flaws and stresses originating from the bonded interface rather than from functional surfaces (Thompson and Anusavice, 1994).

A resin coating technique was introduced for indirect restorations to minimize pulpal irritation and postoperative sensitivity (Momoi, 2003). This technique also enables better bonding, sealing, and adaptation to dentin (Peters and McLean, 2001).

Resin coating in combination with a dentin adhesive system and a low-viscosity microfilled resin has been recommended for the prepared cavity immediately after tooth preparation, just before taking a final impression. This technique provides a hybrid layer and a tight sealing film on the dentin surface (Jayasooriya *et al.*, 2003). However, the combination of a dentin bonding system and a low-viscosity microfilled resin creates a layer of more than 100 μm thickness on the

dentin surface, which is too thick for coating of crown preparations (Jayasooriya *et al.*, 2003). It was reported that the thin-film coating material could prevent marginal leakage beneath full cast crowns (Kosaka *et al.*, 2005).

Moreover, clinically cemented restorations are subjected to repeated matiscatory forces under dry and wet conditions; therefore, this environment should be replicated during *in vitro* testing of such restorations (Ohyama *et al.*, 1999; Gu and Kern, 2003).

Bond strength and leakage studies have been used individually as in vitro indicators of both retention and marginal sealing abilities of composite restorations. However, to the authors' knowledge, no information is available regarding the effect of resin coating and occlusal loading on the adhesion and microleakage of all-ceramic crowns fabricated with CEREC 3.

Therefore, the purpose of this in vitro study was to evaluate the microtensile bond strength of a resin cement to dentin and ceramic using a resin coating technique on the prepared teeth, and the microleakage of CAD/CAM fabricated all-ceramic crowns, and also to evaluate the influence of occlusal loading. The null hypothesis proposed were: (1) applying a resin coating did not affect the adhesion and the microleakage of all-ceramic crowns, and (2) occlusal loading did not affect the adhesion and the microleakage of all-ceramic crowns.

Materials and Methods

Specimens

Twenty-eight non-carious human lower third molars, extracted in accordance with the local ethical committee rules, were used in this study. The root of each specimen was dipped up to 1mm below the cement-enamel junction in a two-part silicone model duplicating material (SP8016 Hard; Bracon Dental Laboratory Products, E. Sussex, UK) which was left to dry, so that each root was surrounded by a simulated periodontal

membrane. Then the root base of each tooth was embedded in acrylic resin (Mr Dental, Cold Cure Modeling Acrylic; Meadway, Surrey, UK) for stabilization of the tooth.

Preparation design

Figure 1 illustrates the specimen preparation. Each tooth was prepared to receive an all-ceramic crown using a diamond bur mounted on a high-speed hand piece under water coolant. The tooth preparation design was the same as that used for all-ceramic crowns (Shillinburg *et al.*, 1997). Occlusal reduction of approximately 2.0 mm from the central groove was performed using a wheel-shaped diamond bur (FG 845C; Sybron Kerr Corp., CA, USA). Following this, axial reduction was performed with a circular 1 mm-deep shoulder finish line placed on the enamel using a flat end tapered diamond bur (FG 740R; Sybron Kerr Corp.). All line angles were smoothed to reduce the possibility of stress concentrations. The prepared tooth surfaces were also examined with a stereo-microscope (SDZ-PL; Kyowa Optical Co., Kanagawa, Japan) to ensure that occlusal surfaces were free of enamel.

All the prepared teeth were randomly divided into two groups of fourteen teeth each, according to whether the tooth was to be resin-coated or not.

Materials used in this study

The resin coating material and the resin cement used in this study are listed in Table 1. For the resin coating, Clearfil Tri-S Bond (Kuraray Medical, Tokyo, Japan) was used. Clearfil Tri-S Bond is a self-etching, one-bottle bonding agent which contains an acidic monomer, 10-methacryloyloxy-decyl dihydrogenphosphate, MDP. A dual-cured resin cement, Clearfil Esthetic Cement (Kuraray Medical) was used for cementation. The self-etching primer, ED Primer II (Kuraray Medical), is the self-etching system used with Clearfil Esthetic Cement.

Table 1. Resin coating material and resin cement used in this study

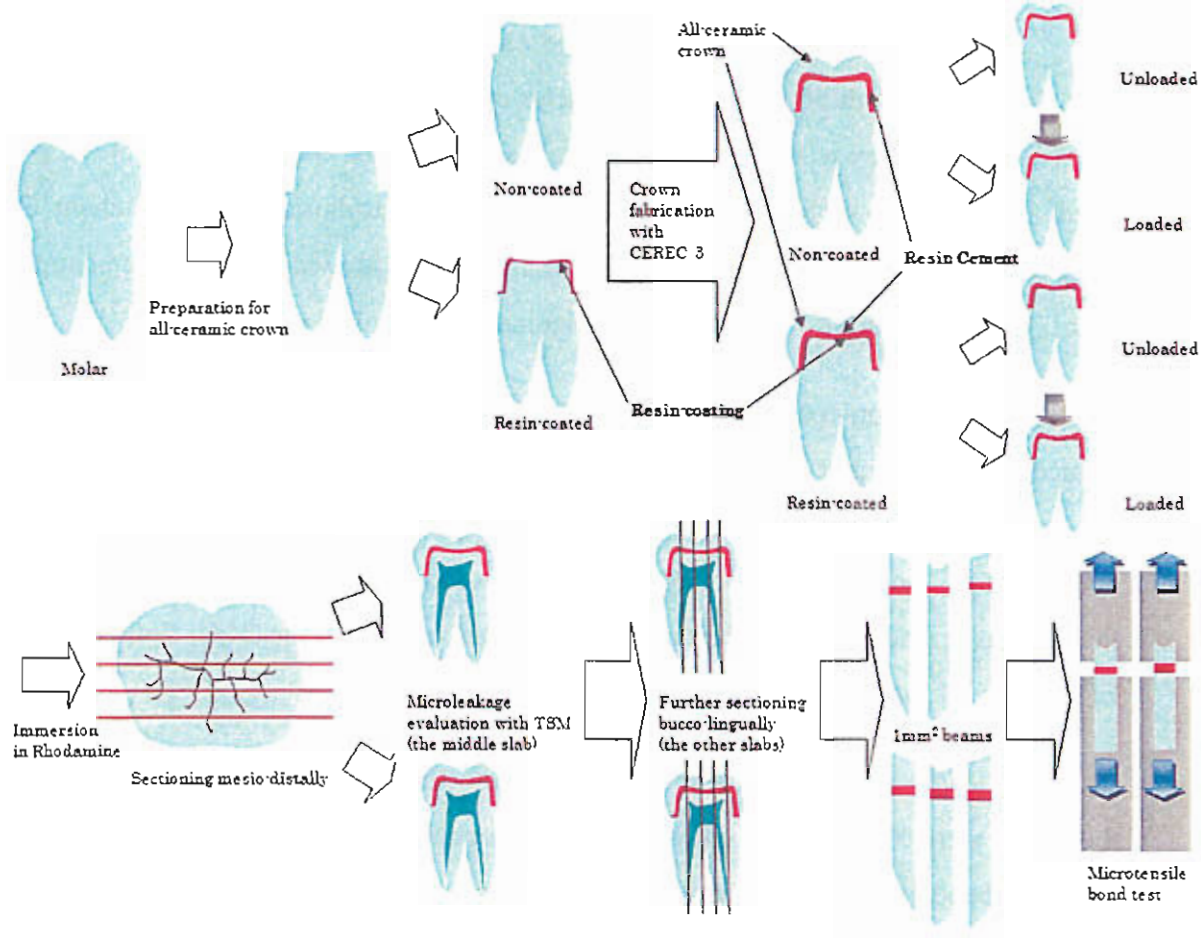
Material	Batch No.	Composition
Clearfil Tri-S Bond	00085A	Bis-GMA, MDP, HEMA, Hydrophobic dimethacrylate, Silanated colloidal silica, dl-Camphorquinone, Ethyl alcohol, Water
K Etchant Gel	00402A	Phosphoric acid, Colloidal silica, Pigments, Water
Clearfil Ceramic Primer	00004E	3-trimethoxysilylpropyl methacrylate, MDP, Ethanol
Clearfil Esthetic Cement	00239A	ED Primer Ⅱ A: HEMA, MDP, Accelerator, Water
	00117A	ED Primer Ⅱ B: Methacrylate monomers, Initiator, Accelerator, Water
	0004BB	Paste A: Bis-GMA, TEGDMA, Other methacrylate monomers, Silanated glass filler, Colloidal silica
	0004BB	Paste B: Bis-GMA, TEGDMA, Other methacrylate monomers, Silanated glass filler, Silanated silica, Colloidal silica, Benzoyl peroxide, dl-Camphorquinon, Pigments

Bis-GMA, bisphenol A diglycidyl ether dimethacrylate;
MDP, 10-methacryloyloxy-decyl dihydrogenphosphate;
HEMA, 2-hydroxyethyl methacrylate;
TEGDMA, triethyleneglycol dimethacrylate
Manufacturer: Kuraray Medical, Tokyo, Japan

Resin coating

For the non-coating group, the prepared surfaces were left as a control. For the resin-coating group, Clearfil Tri-S Bond was applied to the prepared surface for 20 seconds and light-cured for 30 seconds in total, 10 seconds each from occlusal, buccal and lingual directions, using a visible light curing unit (Optilux 501; Sybron Kerr Corp., CA, USA). Following this, Clearfil Tri-S Bond was applied and light-cured again to the coated surface in the same way as described above.

Figure 1. Illustration of specimen preparation.



Crown fabrication with CAD/CAM

Imaging propellant (VITA CEREC Propellant; VITA Zahnfabric, Bad Säckingen, Germany) and powder (VITA CEREC Powder; VITA Zahnfabric) were applied to the tooth and optical impressions were taken using CEREC 3. Using the CEREC 3 software, twenty-eight crowns were designed, and milled from CEREC-Blocs (Sirona Dental Systems GmbH) using the CEREC 3 milling unit.

Cementation procedures

After the optical impressions, the teeth were cleaned with isopropyl alcohol to remove the imaging powder. The cementation procedures were performed according to the

manufacturer's instructions.

Regarding the pretreatment for the all-ceramic crowns, the internal surfaces were air-abraded with 50 μm alumina particles at 0.15 MPa for 10 seconds at a distance of 10 mm. Then they were ultrasonically cleaned in distilled water for 5 minutes and air dried. The internal surfaces were etched with 37% phosphoric acid (K Etchant Gel; Kuraray Medical) for 10 seconds, rinsed and air dried. Following this, a silane coupling agent (Clearfil Ceramic Primer; Kuraray Medical) was applied and air dried.

For the non-coated teeth, the enamel and dentin surfaces to be bonded were primed with ED Primer Ⅱ for 30 seconds. For the resin-coated teeth, the surfaces to be bonded were pre-treated as follows: the surfaces were etched with K Etchant Gel for 5-10 seconds, rinsed and air dried in order to remove debris. Then Clearfil Ceramic Primer was applied to the etched surfaces for silanization and air dried. Following this, ED Primer Ⅱ was applied for 30 seconds and air dried.

Clearfil Esthetic Cement was placed onto the internal surfaces of crowns and then they were seated and light-cured for 60 seconds in total, 20 seconds each from occlusal, buccal and lingual directions. The bonded specimens were stored in 37 ℃ distilled water for 24 hours.

Occlusal loading

After the cementation procedure, the teeth from both non-coated and resin-coated groups were further divided into two subgroups of seven teeth each according to whether the tooth would be loaded or not. The teeth for loading were mounted in a customized jig for loading by a linear actuator (LAL90; SMAC Europe Ltd., Horsham, UK). Oral mechanical stress was stimulated at a rate of 2.5 loads per seconds for 250,000 cycles with a load of 80 N in a water bath maintained at 37 ℃. The load force was applied parallel to the long-axis of the tooth at the central groove using a 2 mm wide, round ended, stainless steel shaft. The unloaded teeth were stored in distilled water at 37 ℃ for an equivalent time span which was approximately 28 hours (Bravis *et al.*, 2008).

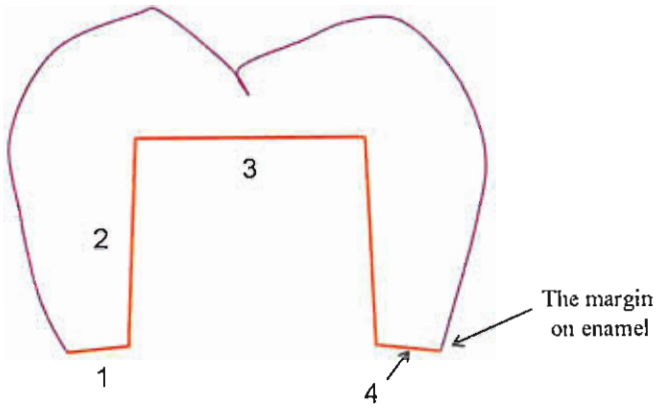
Microleakage evaluation

After occlusal loading, the teeth were carefully pulled out of the acrylic resin. For evaluation of microleakage, the teeth were sealed with two coats of nail varnish up to within 1.0 mm of the cervical margins. Then they were immersed in a 0.25 % solution of rhodamine B in distilled water at 37 ℃ for 24 hours. After that, they were thoroughly rinsed in water and ultrasonically cleaned in distilled water for 5 minutes.

The teeth were sectioned mesiodistally with a diamond blade (Extec Dia Wafer Blade; Extec Corp., Enfield, CT, USA), providing slabs with a thickness of 1.0 mm each. The slabs obtained from the central regions were used for microleakage evaluation, following polishing with 1000 grit silicon carbide paper (Struers Ltd, Solihull, UK) and ultrasonication.

A confocal microscope of the tandem scanning type (TSM; Noran Instruments, Middleton, WI, USA) was used to focus below the surface smear layer created by sectioning and polishing. Samples were examined using a ×20/0.80 numerical aperture (NA) oil immersion objective in conjunction with a 4912 monochrome CCD camera (Cohu Inc., San Diego, CA, USA) and the image was relayed to a monitor. Dye penetration was observed by use of the appropriate fluorescence excitation and barrier filters (546/600 nm) and measured using a calibrated acetate sheet on the monitor screen. The sites of the measured microleakage were assigned to margin, axial wall and occlusal table (Figure 2). Penetration into the cement-dentin was considered. For the resin-coated group, fluorescence detected between resin cement and resin coating and between resin coating and dentin as well as the fluorescence within resin coating were considered as microleakage because the interface between the cement and the resin coating was indiscernible. For all the observed interfaces, the length of the interface and the length of the dye penetration were recorded, and their ratio was established by site. High resolution reflection and fluorescence images of the interfaces were taken using the same x20 objective but in conjunction with an iXon 885 EM-CCD (Andor Technology, Northern Ireland, UK).

Figure 2. The sites of the measured microleakage



1: margin, 2: axial wall, 3; occlusal table 4, EDJ

Microtensile bond test

The other slabs were further sectioned vertically in a buccolingual direction to obtain beams with an approximate surface area of 1×1 mm^2. The dimensions of each beam were checked with a caliper before the microtensile test.

Following this, each specimen was attached to a customized microtensile jig with cyanoacrylate adhesive (Zapit; Dental Ventures of America, Corona, CA, USA) and mounted on a linear actuator (LAL 300; SMAC Europe Ltd) for microtensile bond strength (MTBS) testing at a crosshead speed of 1mm/min.

Failure mode analysis

The fractured interfaces of the specimens after the microtensile bond test as well as the fractured interfaces of the pre-test failed specimens were determined at a magnification of 45 times using a stereo-microscope (SDZ-PL; Kyowa Optical Co.).

Three representative samples of each fracture mode were selected and examined with an SEM (S-3500N; Hitachi, Tokyo, Japan) after gold sputter coating (E5100; Polaron Equipment Ltd., Hertfordshire, UK) to examine the debonded area.

Statistical analysis

Analysis of variance was performed to assess the effect of resin-coating and loading on the micoleakage for each site and the microtensile bond strength. The number of fractured specimens before and after bond test was analyzed by a chi-square test. Statistical significance for the above statistical tests was predetermined at a 95% confidence level.

Results

Microleakage

The proportion of microleakage at each site is shown in Table 2-4. Loading did not have a significant effect on the microleakage in either the non-coated or resin- coated group. At the margin, resin-coating increased the microleakage for both the unloaded and loaded groups ($p<0.01$). At the axial wall, resin coating increased the microleakage for the unloaded group ($p<0.05$). No other significant difference was observed in either group at the axial wall and occlusal table.

Table 2. The proportion of microleakage at the margin (%)

	Unloaded	Loaded	P value
Non-coated	61.1 (31.8)	66.0 (16.4)	0.620
Resin-coated	93.3 (18.2)	92.4 (17.3)	0.898
P value	0.004	<0.001	

All values are mean (SD).

Table 3. The proportion of microleakage at the axial wall (%)

	Unloaded	Loaded	P value
Non-coated	75.7 (11.6)	75.4 (28.2)	0.966
Resin-coated	86.4 (10.8)	82.2 (8.3)	0.266
P value	0.021	0.393	

All values are mean (SD).

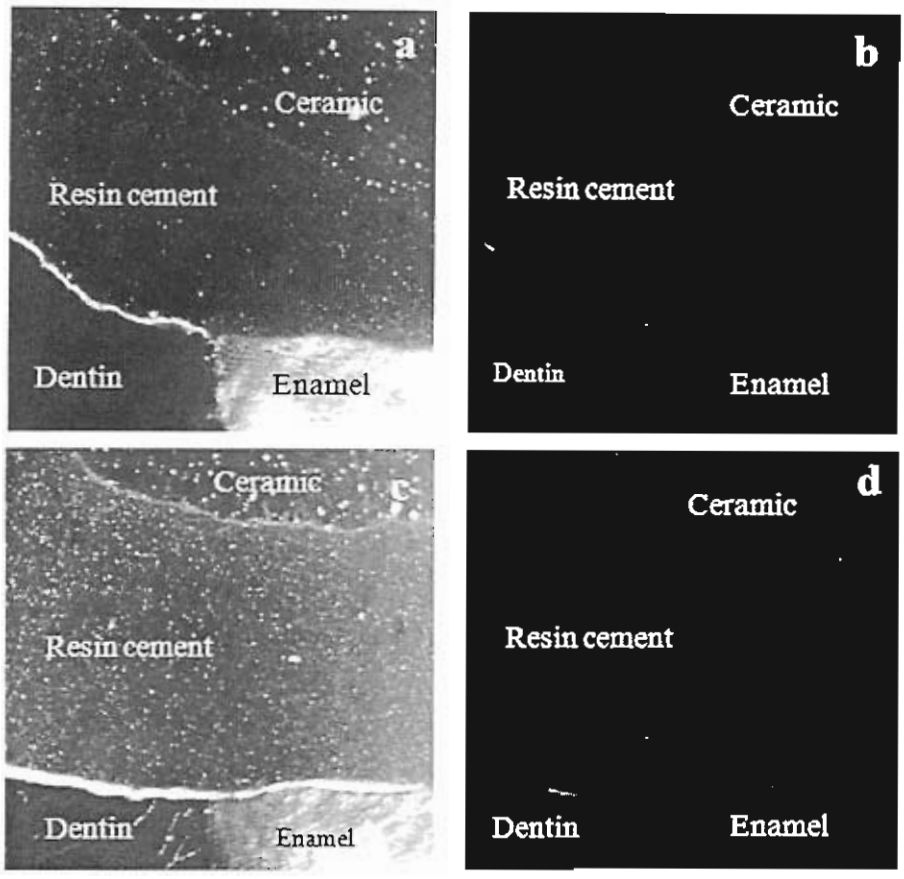
Table 4. The proportion of microleakage at the occlusal table (%)

	Unloaded	Loaded	P value
Non-coated	49.7 (27.7)	51.2 (21.8)	0.871
Resin-coated	45.7 (24.4)	37.4 (24.0)	0.372
P value	0.688	0.130	

All values are mean (SD).

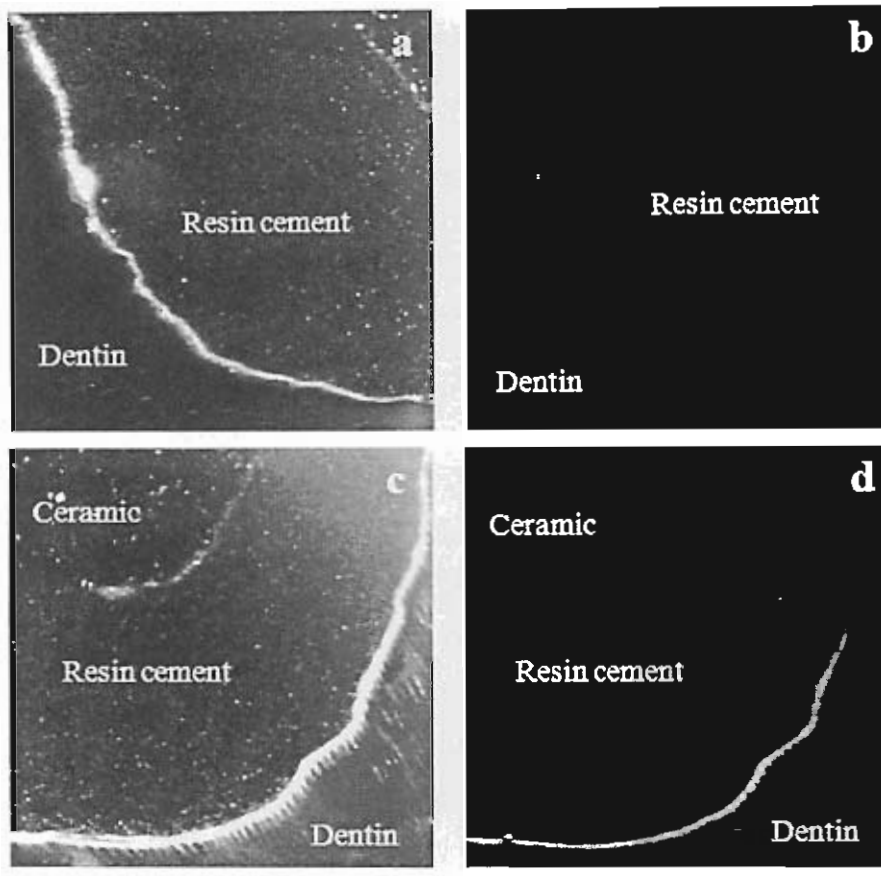
Figures 3 - 6 show the TSM images of microleakage of the specimens after loading for each site. At the enamel in the margin, the majority of the non-coated teeth showed minimum leakage whereas that of resin-coated teeth showed extensive amounts of leakage (Figure 3). At the line angle of margin and axial wall, and the axial wall, both non-coated and resin coated tooth showed microleakage at the dentin (Figures 4 & 5). At the occlusal table, less leakage was observed compared to other sites (Figure 6).

Figure 3. Confocal micrographs of microleakage of loaded specimens. Images of microleakage located at the EDJ.



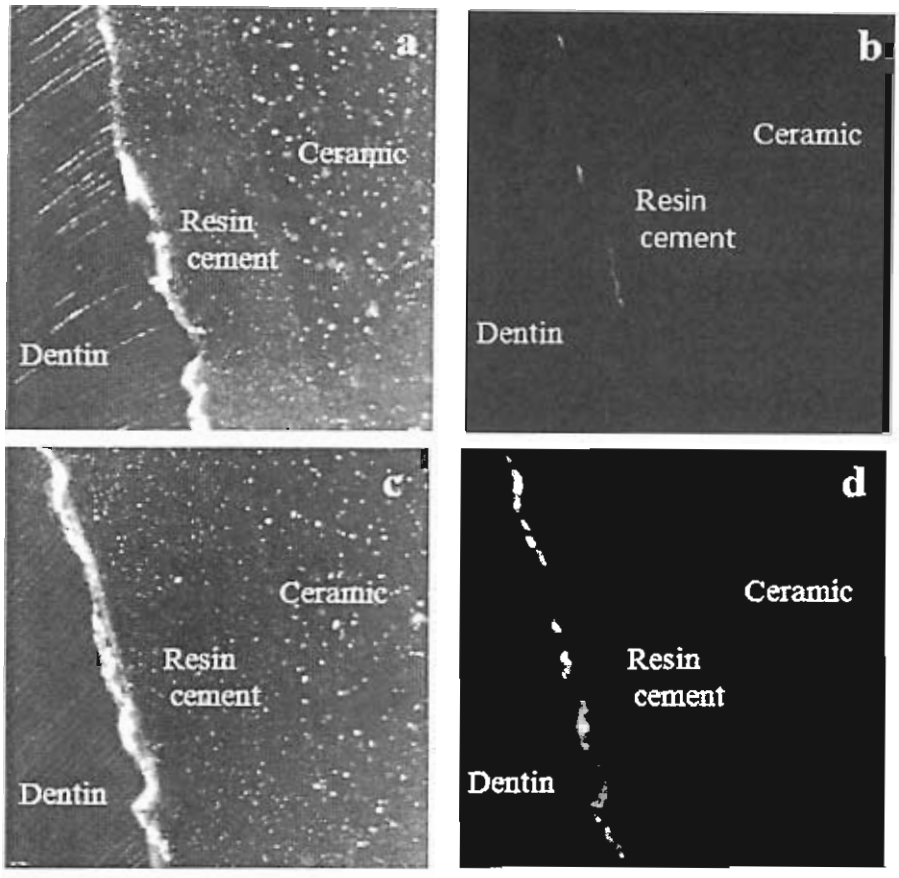
(a) and (c) show reflection images of non-coated and resin-coated teeth, respectively. Fluorescence images show no leakage at the enamel in the non-coated tooth (b) whereas leakage was observed at the enamel in the resin-coated tooth (d). Tandem scanning confocal microscope (TSM) x20/0.80 NA oil immersion objective. 546/- nm (a & c) 546/600 nm (b & d). Fieldwidth 400 μm.

Figure 4. Confocal micrographs of microleakage at the line angle of the margin and axial wall.



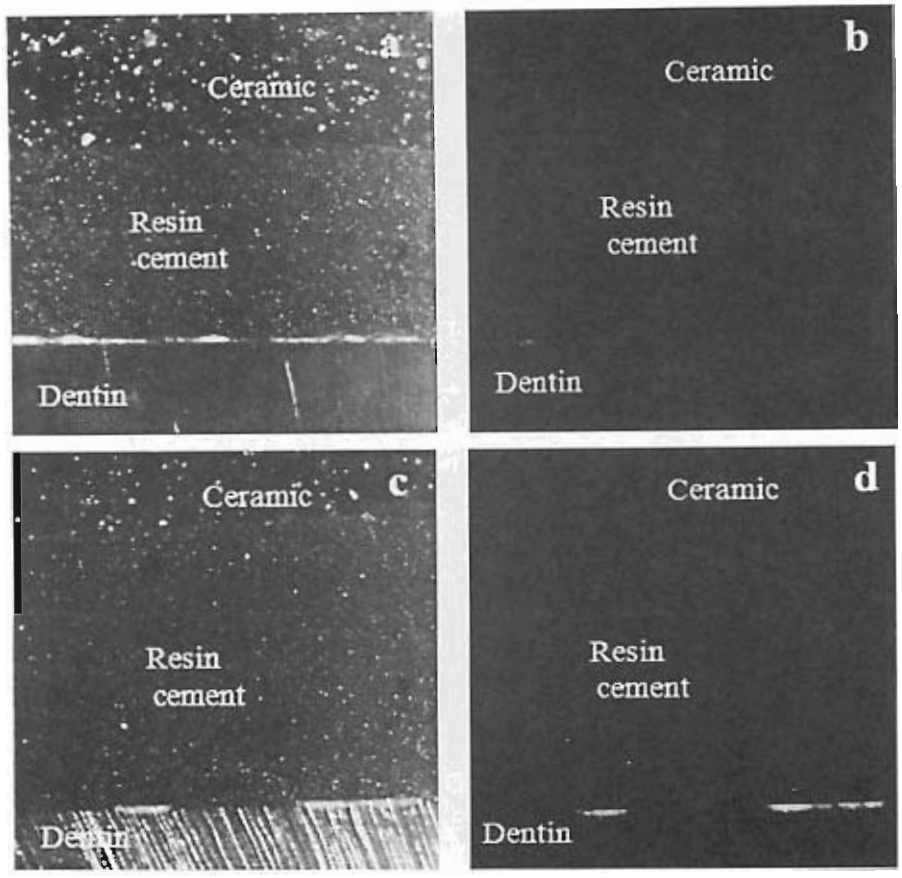
(a) and (c) show reflection images of non-coated and resin-coated teeth, respectively. Fluorescence images show leakage in both the non-coated (b) and resin-coated (d) teeth. TSM x20/0.80 NA oil immersion objective. 546/- nm (a & c) 546/600 nm (b & d). Fieldwidth 400 μm.

Figure 5. Confocal micrographs of microleakage at the axial wall.



(a) and (c) show reflection images of non-coated and resin-coated teeth, respectively. Fluorescence images show leakage in both the non-coated (b) and resin-coated (d) teeth. TSM x20/0.80 NA oil immersion objective. 546/- nm (a & c) 546/600 nm (b & d). Fieldwidth 400 μm.

Figure 6. Confocal micrographs of microleakage at the occlusal table.



(a) and (c) show reflection images of non-coated and resin-coated teeth, respectively. Fluorescence images show leakage in both the non-coated (b) and resin-coated (d) teeth. TSM x20/0.80 NA oil immersion objective. 546/- nm (a & c) 546/600 nm (b & d). Fieldwidth 400 μm.

Microtensile bond strength

The number of fractured specimens before and after bond testing in each group is shown in Table 5 and 6. Mean microtensile bond strength, standard deviation, total number of specimens and number of tested specimens are summarized per group in Table 7. When non-coated and loaded, all the beams fractured during slicing for bond strength testing. When unloaded, there was no significant difference in microtensile bond strength between the non-coated and resin-coated groups ($p=0.334$). When resin-coated, the mean microtensile bond strength did not significantly decrease after loading ($p=0.075$).

Table 5. The number of fractured specimens before and after bond test in unloaded and loaded groups

		Failure time		
		Before test	After test	Total number
Unloaded*	Non-coated	33	45	78
	Resin-coated	32	49	81
Loaded**	Non-coated	89	0	89
	Resin-coated	38	60	98

Failure before vs after bond test: * $p=0.719$, ** $p<0.001$

Table 6. The failure mode distribution of the unloaded and loaded groups (number of beams)

		Failure mode					
		Before test			After test		
		1	2	3	1	2	3
Unloaded	Non-coated	33	—	0	45	—	0
	Resin-coated	22	10	—	40	9	—
Loaded	Non-coated	15	—	74	0	—	0
	Resin-coated	24	14	—	57	3	—

Table 7. Microtensile bond strength (MPa).

	Unloaded	Loaded	P value
Non-coated	15.82±4.22 (45/78)	— (0/89)	—
Resin-coated	15.17±5.24 (49/81)	12.97±5.82 (60/98)	0.075
P value	0.334	—	

Mean±SD (number of beams, tested/total).

Failure mode analysis

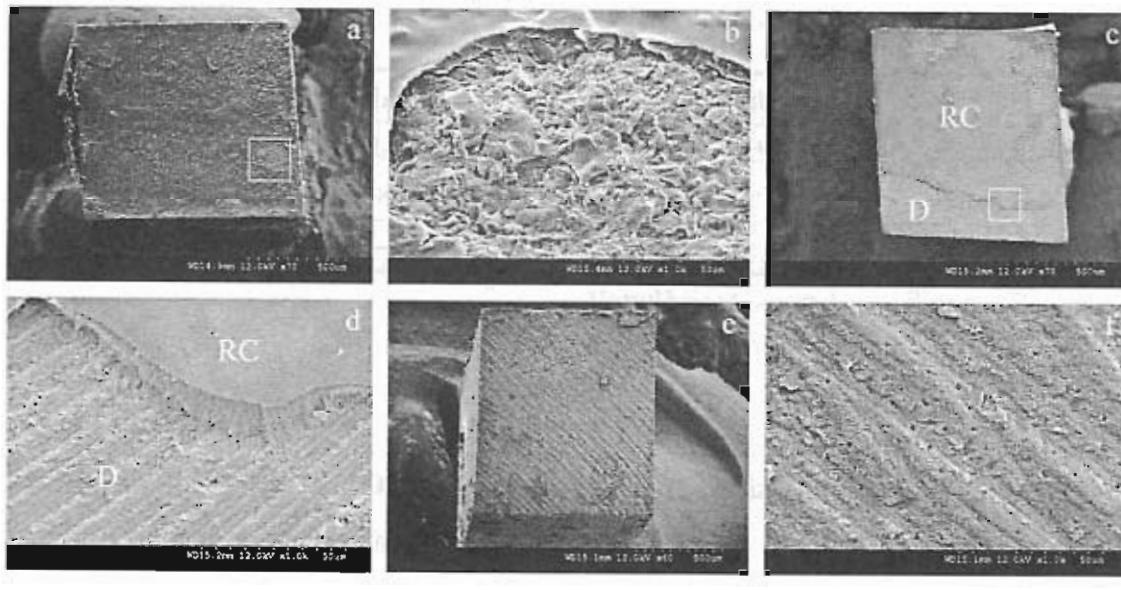
The failure modes were classified as follows: more than 80% adhesive failure between ceramic and cement and less than 20% cohesive failure in cement (mode 1), adhesive failure between cement and resin coating and adhesive failure between resin coating and

dentin (mode 2), or more than 80% adhesive failure between cement and dentin and less than 20% cohesive failure in dentin (mode 3).

The number of fractured specimens before and after bond testing in the unloaded and loaded groups is shown in Tables 5. The failure mode distribution of the unloaded and loaded groups is shown in Tables 6. The predominant failure mode of non-coated and unloaded, resin-coated and unloaded, and resin-coated and loaded groups was mode 1 (i.e. more than 80% adhesive failure between ceramic and cement) whereas that of non-coated and loaded pre-test failures was mode 3 (i.e. more than 80% adhesive failure between cement and dentin). The Chi-square test revealed that there was no significant difference in the failure mode before and after bond testing between the non-coated and resin-coated groups in the unloaded group ($p=0.719$) whereas there was a significant difference in the failure mode before and after bond testing between the non-coated and resin-coated groups in the loaded group ($p<0.01$).

Figure. 7 shows the SEM images of typical fractured beams of each failure mode. Scratch marks remaining from dentin preparation confirmed that the failure occurred at the interface either between cement and dentin or between resin coating and dentin.

Figure 7. SEM images of each failure mode



(a) The cement side of a failure mode 1 specimen. The specimen mostly failed at the interface between ceramic and cement. (×70)

(b) Higher magnification of the area marked in (a). Cohesive failure in resin cement could be observed. (×1000)

(c) The dentin side of a failure mode 2 specimen. The failure was located either at the interface between cement and resin coating (RC) or between resin coating and dentin (D). (×70)

(d) Higher magnification of the area marked in (c). A few patent tubules could be observed. The thin layer of resin coating remaining on the dentin could be observed. (×1000)

(e) The dentin side of a failure mode 3 specimen. The specimen mostly failed at the interface between cement and dentin. (×60)

(f) Higher magnification of the failure surface in (e). Many tubles were open and the others were filled with resin tags or smear plugs. (×1000)

Discussion

Resin coating

Clearfil Tri-S Bond has been reported to produce a thin coating layer (Kaneshiro *et al.*, 2008). This might be explained by the strong air-drying necessary during the application. The resin coating for crown preparations should be thin, as a thick coating may adversely affect the fit of the crown. In the present study, Clearfil Tri-S Bond was used as a resin coating material in combination with Clearfil Esthetic Cement.

A single application of a dentin bonding agent (DBA) to the prepared cavity has been shown to protect the exposed dentin and prevent postoperative sensitivity (Christensen, 2000). Paul and Schärer (Paul *et al.*, 1997) recommended a dual application of the DBA, in which the same DBA was reapplied before adhesive cementation of the final restoration. The dual application of the DBA demonstrated as a beneficial effect, the bond strength of indirect restoration to dentin surfaces (Bertschinger *et al.*, 1996; Nikaido *et al.*, 1997). Therefore, Clearfil Tri-S Bond was

reapplied and light-cured immediately after the first application and light-curing to the prepared surface.

Occlusal loading

The effect of mechanical loading was examined due to its potential for simulating matiscation (Abdalla *et al.,*. 1996; Darbyshire *et al.*. 1997; da cunha Mello *et al.,* 1997; Prati *et al.,* 1994). A force of 80 N was chosen as an average of the matiscatory forces observed by Anderson (Anderson *et al.,* 1956). The loading conditions with 250,000 cycles have been verified as representing one year of clinical wear (DeLong *et al.*, 1985: Sakaguchi *et al*, 1986).

Microleakage

In the pilot study, a stereomicroscope was used for the evaluation of microleakage as previously reported (Toman *et al.*, 2007; Prati *et al.*, 1994; Deliperi *et al.*, 2007). The majority of the specimens in each group showed no dye penetration using the stereomicroscope. However, the extensive leakage was observed using the TSM in the same specimens. Confocal microscopy can be used to observe thin optical sections below the surface of the specimens (Watson and Boyde, 1987). Moreover, fluorophores can also act as markers for fluid penetration at the interface between the tooth and the restoration (Watson and Boyde, 1987; Chong *et al.*, 1991; Torabinejad *et al.*, 1993). Microleakage studies performed with fluorescent dyes and examined using confocal microscopy may provide a more accurate description of restorative failure (Watson and Boyde, 1991). Therefore the TSM was used in this study.

Loading did not significantly influence the microleakage of both the non-coated and resin coated groups. Several studies have reported that microleakage around restorations is accelerated by mechanical loading (Davidson *et al,*. 1993; Lundin *et al,*. 1991; de cunha Mello *et al,*. 1997). However, other studies have not found a significant effect of loading on microleakage (Darbyshire *et al.,* 1988; Prati *et al.,* 1994; Mitsui *et al.,* 2003; Gu *et al.*, 2003; Arisu *et al.*, 2008). This disagreement may result from differences regarding the testing method and the magnitude of load application. The descriptive hypothesis for the results is that marginal gaps can be transient

(Cardoso *et al.*, 1998; Hanning *et al.*, 1999; de cunha Mello *et al.*, 1997), taking place only at the moment of load application. After that, their initial configuration would be recovered, thus resulting in marginal sealing and microleakage proportions that do not differ from those of the unloaded teeth.

The occlusal stress consisted mainly of vertical forces, although a certain level of horizontal force might be generated because of the inclination of the tooth cusp. A three-dimensional finite element analysis has demonstrated that vertical forces lead to compressive stresses concentrated in the marginal areas, while horizontal loads induce tensile stresses. (Hojjatie *et al.*, 1990). Therefore, under the occlusal loading, the stresses on the marginal areas of crowns must be considered primarily compressive, which tends to "close up" pre-existing gaps at the tooth-restoration interface.

The margin was placed above the CEJ with a width of approximately 1 mm as it would be difficult to scan the subgingival margin in the clinical situations using CEREC 3. Therefore, the marginal site for microleakage evaluation consists of enamel and dentin. The resin coated groups showed significantly greater microleakage than non-coated groups at the margin as resin-coated enamel showed extensive leakage whereas non-coated enamel showed minimum leakage. It was reported that solvated adhesives exhibited extensive amount of water sorption, which was significantly greater than that of the non-solvated adhesives (Malacarne *et a.l*, 2006). Also, the mass of the adhesives greatly increased within the 1st day of water storage, which can be considered due to water sorption. As single-bottle adhesives are intrinsically hydrophilic owing to the presence of acidic, highly polar functional groups substituted on methacrylates, they will rapidly absorb water, which results in polymer swelling, plasticizing (Ito *et al.*, 2005; Malacarne *et al.*, 2006), and weakening of the polymer network (Ito *et al.*, 2005; Yiu *et al.*, 2004). Clearfil Tri-S Bond is also a solvated, single-bottle adhesive; therefore, it is speculated that the resin coating at the enamel absorbed rhodamine solution during the water storage time which was approximately 52 hours (24 hours after cementation and 28 hours during loading). On the other hand, for non-coated teeth, Clearfil Esthetic Cement was directly bonded to the prepared enamel. It seems that the bonding between the prepared enamel and the resin cement was strong and/or the resin cement infiltrated

into the hybridized enamel sufficiently, thus resulting in minimum leakage at the enamel for non-coated tooth.

At the axial wall, there was a significant difference between the non-coated and resin-coated groups in the unloaded condition whereas no significant difference was found between the non-coated and resin-coated groups in the loaded condition. However, each group exhibited a large amount of leakage (more than 75%). It was reported that the self-etching ED primer permits water-induced changes at the dentin-adhesive interface (Carvalho *et al.*, 2004) due to its permeability, which may explain the high proportion of microleakage for the non-coated groups. Also, Clearfil Tri-S Bond is a single-step, self-etching adhesive. Although hydrophobic dimethacrylates are added to this adhesive to produce stronger cross-linked polymer networks, the hydrophilic monomers tend to cluster together before polymerization to create hydrophilic domains (Eliades *et al.*, 2001; Spencer and Wang, 2002) and microscopic water-filled channels called "water trees" (Tay *et al.*, 2002; Ferrari and Tay, 2003). The exsistence of water trees within the adhesive, rendering the adhesive permeable (Pommersheim *et al.*, 1998, Yang *et al.*, 2002), has been demonstrated, which may explain the high proportion of microleakage for the resin-coated groups.

Microtensile bond strength

When unloaded, the failure mode of both non-coated and resin-coated groups was predominantly mode 1 (i.e. more than 80% adhesive failure between ceramic and cement), indicating that bonding between ceramic and cement was weaker than that between cement and dentin in the unloaded condition. This explains why both the non-coated and coated group showed similar bond strengths (15.82 MPa and 15.17 MPa, respectively) regardless of the resin-coating when unloaded.

When loaded, all the beams of non-coated specimens fractured during slicing whereas most beams of the resin-coated specimens survived for bond strength testing. The predominant pre-test failure mode of the non-coated group was mode 3 (i.e. more than 80% adhesive failure between cement and dentin), indicating that the interface between cement and dentin was more susceptible to deterioration by occlusal loading in

the non-coated group. On the other hand, the predominant failure mode of the resin-coated group was mode 1 (i.e. more than 80% adhesive failure between ceramic and cement), indicating that a thin layer of resin coating created with a dual application of Clearfil Tri-S Bond improved the bonding between cement and dentin, thus the failure mode resulted in mode 1. Several studies (Islam *et al.*, 2006, Nikaido *et al.*, 2003 2003) reported that a thin layer of resin coating with a one-step self-etch adhesive improved the bonding between indirect composite and dentin. However, to the authors' knowledge, no scientific data are available concerning the effect of resin coating on bond strength after occlusal loading. The results of the present study suggest that resin-coating improved the bonding durability of all-ceramic crowns cemented with a resin cement against occlusal loading.

When resin-coated, the mean microtensile bond strength did not significantly decrease after loading ($p=0.075$). However, a trend towards loading having an effect on the microtensile bond strength in the resin-coated group was observed.

It was reported that the majority of failures of a ceramic block bonded to flat dentin with resin cement (approximately 65%) occurred adhesively between ceramic and cement under conditions of either water storage or mechanical loading for 10 weeks (Hernandez *et al.*, 2008). The authors suggested that during the initial period after restoration cementation, the weak link in the interface occurs between the ceramic and the cement. This is in agreement with the present study only when unloaded, although the water storage period in the present study was approximately 2 days and shorter compared to that by Hernandez *et al.* The authors also suggested that the mode of failure was not influenced by normal molar masticatory forces. This is in disagreement with the present study since the non-coated and loaded group failed adhesively between cement and dentin during slicing. This disagreement may be explained due to differences of sample preparation, pretreatment of ceramic, resin cement, and methodology of loading in terms of cycle, force and length.

The results of this study were characterized by a high incidence of specimens that presented premature de-bonding and, consequently, were not subjected to the microtensile bond strength test. We speculate that this could be explained by the

possible low bond strengths obtained in this study and by the small size and fragility of specimens. Ermis *et al.* (Ermis *et al.*, 2008) also found high incidence of premature failures when testing microtensile bond strength of either Adper Prompt L-Pop or Clearfil Tri-S Bond to exposed flat dentin. It is possible that the sectioning process itself may have some detrimental effect on the measured bond strength. Furthermore, when the interface has been weakened from occlusal loading, this effect may be more pronounced.

The clinical relevance of dye leakage studies has been questioned (Wu *et al.*, 1993). No correlation has ever been established between the results of microleakage studies of restorative materials and the prevalence of secondary caries when the same materials were tested under clinical conditions. Moreover, *in vitro* cementing conditions do not completely represent clinical procedures, because *in vivo* oral fluids and pulpal pressure lead to a moist surface (Beschnidt. 1999), which can reduce the adhesion of cements. Therefore, the clinical relevance of the results of this study remains questionable although all experimental groups showed extensive leakage. On the other hand, microleakage tests can evaluate the ability of restorative materials to prevent fluid penetration (Mannocci *et al.*, 2001).

Further studies using different adhesives including hydrophobic varieties need to be conducted in order to investigate the effect on microleakage. In addition, the long-term durability of resin coating also need to be evaluated in terms of mechanical properties, bonding and microleakage.

Conclusions

Within the limitations of this study, it may be concluded that resin coating with Clearfil Tri-S Bond increased the bonding durability of the resin cement to dentin against occlusal loading *in vitro*. However, it was not effective in reducing the microlakage, but increased the microleakage at the margin placed on the enamel, whether loaded or unloaded.

Chapter 6

General conclusions

Chapter 1 concluded that self-etching adhesives showed more stable bond strengths to ground enamel after thermal cycling than the phosphoric acid-etching adhesives. In addition, with self-etching adhesives, problems concerning the decalcification of and damage to the enamel surface were eliminated.

Chapter 2 came to the conclusion that conditioning the zirconia surface with a primer containing acidic monomer was effective in improving the bonding of resin cements to zirconia ceramics. However, the effectiveness was material dependent.

Chapter 3 concluded that the coating of the zirconia surface by fusing silica-based ceramics followed by silanization significantly increased the initial bond strength of resin cements to zirconia surface.

Chapter 4 showed that the coating of the zirconia surface with veneering porcelain followed by silanization showed significantly higher bond strength of a resin cement to zirconia than the non-coated zirconia conditioned with an acidic-monomer containing primer, before and after thermal cycling. However, the bond strength siginificantly decreased for both non-coated zirconia and porcelain-coated zirconia after thermal cycling.

Chapter 5 showed that resin coating with Clearfil TriS-Bond increased the bonding durability of the resin cement to dentin against occlusal loading. However, it was not effective in reducing the microlakage, but increased the microleakage at the margin placed on the enamel, whether loaded or unloaded.

In the study in Chapter 1, although self-etch adhesives performed well compared to phosphoric acid-etch adhesives, the ground enamel was used instead of unground enamel in order to standardize the bonding surface. Therefore, the effect of self-etch adhesive on intact enamel should be investigated in the future. According to

the results of Chapter 2, 3 and 4, the coating of the internal surface of the zirconia restoration improves the bonding of a resin cement to zirconia. The coating may be used to repair the gap or chipping of the zirconia frame, however, it may not be applicable when the restoration fits the model. The laboratory technique to fuse the porcelain to the internal surface of the zirconia restoration with an adequate thickness should be developed in the future. In the study in Chapter 5, resin coating with Clearfil Tri-S Bond increased the bonding of the resin cement to dentin, but did not reduce the microleakage. Since Clearfil Tri-S Bond is a solvated, single-bottle adhesive which is intrinsically hydrophilic, it may have absorbed the dye during water storage. Further studies should be conducted to investigate the effect of resin coating with different adhesives including hydrophobic varieties on microleakage.

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