Adhesion of dual-cure resin cement to ceramic: Action of ceramic primers

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Preface

This thesis is based on the following original papers, which are referred to the text by the respective chapters.

Chapter 1. Foxton RM, Pereira PNR, Nakajima M, Tagami J, Miura H. Effect of light source direction and restoration thickness on tensile strength of a dual-curable resin cement to copy-milled ceramic. *American Journal of Dentistry* (in press).

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Chapter 3. Foxton RM, Pereira PNR, Nakajima M, Tagami J, Miura H. Long term durability of the dual-cure resin cement/silicon oxide ceramic bond. *The Journal of Adhesive Dentistry* 4: 125-135, 2002.

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Introduction

Bonding of resin cements to ceramic first became a clinical reality when separate studies by Paffenbarger and Semmelman in the late 1960s' showed that acrylic resin could be chemically bonded to porcelain teeth using a silane coupling agent (Paffenbarger et al., 1967, Semmelman and Kulp, 1968). The silane agent used was γ-methacryloxy-propyltrimethoxysilane (γ-MPS). However, in order for the silane to be able to bond to the porcelain surface, it had to be first hydrolysed using a separate acid solution (Paffenbarger et al., 1967).

In the late 1970s, the first in-vitro study on the bonding of composite resin to porcelain was carried out (Newburg and Pameijer, 1978). The authors showed that composite resin could be chemically bonded to porcelain using the silane coupling agent, γ-MPS, which had been hydrolysed using acetic acid. This opened the way for the intra-oral repair of fractured porcelain restorations using a composite resin and a silane coupling agent (Eames et al., 1977; Eames et al., 1979). However, later research by Nowlin et al showed that the same composite/ porcelain bond was not durable and this clinical procedure should be regarded as a temporary treatment (Nowlin et al., 1981).

It was also in the late 1970s, that a clinical technique to restore malformed and discoloured teeth was described by Faunce and Myers in which preformed acrylic laminates were bonded to teeth using composite resin (Faunce and Myers, 1976). However, the chemical bond between the acrylic resin and composite resin was proven to be a weak link leading to numerous failures (Faunce and Myers, 1976). To overcome this problem and also the compromised esthetics of acrylic laminate veneers, a new clinical treatment was introduced, the acid etched porcelain laminate veneer (Calamia, 1985). Simonsen and Calamia reported that a strong resin/ porcelain bond could be achieved if the porcelain surface was etched with hydrofluoric acid (Simonsen and Calamia, 1983). If the etched porcelain surface was further treated with a silane coupling agent, bond strengths could be further enhanced (Calamia and Simonsen, 1984). This is because in feldspathic and lithium silicate ceramics, a glass phase is present which can be etched with hydrofluoric acid. The crystallites are exposed leaving a micromechanically retentive surface. Silanization of the etched surface increases wettability and bond strength. This chemical reaction can only occur if a silicon oxide phase is present and cannot therefore take place in high strength alumina or zirconia ceramics. However, hydrofluoric acid is a hazardous substance and some clinicians are suggesting that its use be curtailed (Peutzfeld, 2001).

In the mid 90s, a new generation of ceramic primers were developed for coupling resin to ceramic, in particular silicon oxide ceramic, and introduced onto the Japanese dental market. These ceramic primers generally consist of two or three solvents, one of which contains a silane coupling agent, usually γ-methacyloxylpropyl-trimethoxysilane (γ-MPS), and the other, an acidic monomer to catalyse the coupling reaction. The solvent is usually either water or an organic solvent such as ethanol, and may also contain the hydrophilic monomer, HEMA. This new generation of liquid ceramic surface treatments have been shown to strongly couple resin to fired porcelain and machinable ceramic without prior sandblasting or hydrofluoric acid etching of the ceramic surface (Aida M et al., 1995; Barghi N et al., 2000; Berry T et al., 1999; Matsumura H et al. 1997; Sato K et al., 1999). Since some of these ceramic primers consist of either a self-etching primer or a dentin bonding agent, and a separate silane coupling agent, there is an advantage of chairside convenience when cementing a ceramic restoration in that, by the simple addition of one solution, the same self-etching primer used for priming the dentin and enamel of the prepared cavity can become a primer for the ceramic restoration.

Regarding the appropriate cement for luting ceramic restorations, dual-cure resin cement is frequently chosen because of the extended working time and controlled polymerization through the inclusion of both chemical and photoinitiators (Cook and Standish, 1983; Krämer *et* al., 2000). However, there are several important factors that might affect the bond between dual-cure resin cement and ceramic when a multicomponent ceramic primer is used, which have not been previously investigated and are discussed in the following chapters as outlined below:

In chapter one, the effects of applying the light-curing tip from different curing directions and the thickness of the ceramic restoration on the strength of the dual-cure resin cement/ceramic bond are evaluated and discussed.

In chapter two, the effects of either, polymerising the dual-cure resin cement chemically or by exposure to light, on the durability of dual-cure resin cement/ceramic bond are evaluated and discussed.

In chapter three, the long-term durability of the dual-cure resin cement/silicon oxide bond when different multicomponent ceramic primers are used, is evaluated and discussed.

In chapter four, the relationship between the ceramic primer and ceramic surface pH on dual-cure resin cement/ceramic bond strength is evaluated and discussed.

In chapter 5, the overall conclusions of the present work and directions for future research are discussed.

Chapter 1

Effect of light source direction and restoration thickness on tensile strength of a dual-curable resin cement to copy-milled ceramic

Introduction

Advances in ceramic milling technology have lead to the machining of ceramic inlays, ceramic veneers, crowns and short-span bridges by either computer-aided design/computer-aided manufacturing (CAD/CAM) or copy-milling (Mörmann and Bindl, 2000; Roulet and Degrange, 1996; Eidenbenz *et al.*, 1994). CAD/CAM systems utilize sophisticated technology to acquire information on the prepared tooth, design and fabricate the restoration (Roulet and Degrange, 1996). Copy-milling on the otherhand, does not use CAD/CAM technology. An intermediary unit fabricated directly on the tooth or a master die, is mechanically traced using a stylus (Eidenbenz *et al.*, 1994). The stylus has a fixed relationship with a turbine which mills the restoration as tracing proceeds Roulet and Degrange, 1996; Eidenbenz *et al.*, 1994). Both CAD/CAM and copy-milling processes use similar feldspathic ceramic blanks or pre-sintered aluminium oxide blocks in order to fabricate a restoration (Goldstein, 1998).

Dual-cure resin cements are frequently chosen for luting these ceramic restorations (Bergman, 1999; Thordrup *et al.*, 1999), because the cements provide extended working times and controlled polymerization through the inclusion of both chemical and photoinitiators (Cook and Standish, 1983; Krämer *et al.*, 2000). For dual-cure resin cement to possess good mechanical properties and bonding capability, a high degree of polymerization is necessary (Harashima *et al.*, 1991; Althoff and Hartung *et al.*, 2000). This level is achieved by applying light to activate the photoinitiators and start polymerization (Stansbury *et* al., 2000). However, previous research demonstrated that both ceramic shade and thickness, and exposure duration alter the quantity of light reaching the resin-, 1989; Blackman *et al.,* 1990). In the absence of light, polymerization must start by chemical initiation, which may result in the dual-cure resin cement having poorer mechanical properties (El-Mowafy *et al.,* 1999), and bonding capability. Previous research has shown that in the absence of light exposure, there is a large variation in the ability of dual-cure resin cements to reach a high level of cure (Rueggeberg and Caughman, 1993) and that they cannot reach maximum hardness by chemical-cure alone (El-Mowafy *et al.,* 1999; El-Badrawy and El-Mowafy, 1995). When dual-cure resin cements were exposed to light, it was reported that after 24 h, the hardness of all tested dual-cure resin cements exposed to light were significantly higher than those which were not (El-Mowafy *et al.,* 1999; El-Badrawy and El-Mowafy, 1995). Furthermore, when dual-cure resin cement was exposed to light from only one direction through feldspathic porcelain and glass-ceramic, 0.5 and 1 mm thick respectively, maximum hardness was attained after 60 s exposure (Blackman *et al.,* 1990). Hardness did not increase even when the exposure time was lengthened to 120 s (Blackman *et al.,* 1990). In addition, it was reported that when a light source is applied to ceramic for 60 s from one direction, significant reductions in dual-cure resin cement hardness occur when ceramic thickness exceeds 2 mm (El-Mowafy *et al.,* 1999).

The bond strength between resin cement and ceramic is commonly evaluated by either shear or tensile bond strength tests. However, recently the validity of these conventional tests, particularly the shear test, has been questioned on the basis that specimens tended to exhibit cohesive failure within the ceramic substrate rather than at the bonded interface (Della Bona and Van Noort, 1995; Chadwick *et al.,* 1998). Since composite resin-ceramic specimens separate more frequently at the bonded interface when subjected to tensile loading, this test procedure may be a more appropriate choice for evaluating resin-ceramic bond strengths (Della Bona and Van Noort, 1995).

The microtensile bond strength test (μTBS test) is a very convenient procedure for evaluating bond strength between resin cement and ceramic. This test procedure has been shown to produce fewer cohesive substrate failures and higher bond strengths when used to evaluate resin-dentin bond strengths (Sano *et al.,* 1994). This result was attributed to the cross-sectional areas of the tested specimens, which are typically 1 mm^2 or less (Sano *et al.,* 1994). Uno *et al.*, 2001, bonded Cerec 2 ceramic to dentin using different dual-cure resin cements and after subjecting the specimens to the μTBS test, found that the specimens failed at either the inlay/resin, resin/dentin interfaces or cohesively in the resin cement in almost equal numbers. When the beam method of specimen preparation is employed (Shono *et al.,* 1999), the μTBS test offers a further advantage over conventional shear and tensile tests. Since the μTBS test does not require bonded ceramic specimens to be embedded in any separate testing apparatus, the bonding interface can be isolated and the direction of any light-source can be easily, and precisely controlled.

When a restoration is luted with dual-cure resin cement, a light source is applied from several directions to ensure that as much light as possible reaches the cement layer (Goldstein, 1998; Thordrup *et al.*, 1999). To date, there is very little information on how exposing dual-cure resin cement to light from several directions as opposed to one direction, actually affects the bond strength between dual-cure resin cement and ceramic and indeed, whether this exposure strategy is always necessary.

The purpose of this study was to evaluate the microtensile bond strength and hardening of dual-cure resin cement when no light-exposure, light-exposure from one direction, and light-exposure from multiple directions were applied to different thickness' of copy-milled ceramic.

Materials and Methods

Ceramic blanks[a], shade A2M, were cut using a horizontal diamond saw[b] under running water, into multiple slices measuring 12 mm x 10 mm x 1 mm, 2 mm, and 3 mm thick. The surfaces of each ceramic slice were carefully polished calipers[c] to ensure their final thickness' were accurate to within 0.1 mm. The thickness of each slice was then measured again using digital using wet 600-grit silicon carbide paper, then cleaned in an ultrasonic water bath for five min. The ceramic slices were then randomly divided into three experimental groups and a control group, as depicted in Figure 1:

Group 1 consisted of six pairs of 1 mm and 3 mm slices; Group 2, six pairs of 2 mm and 3 mm slices; and Group 3, six pairs of 3 mm thick slices. The control group consisted of two pairs of 3 mm thick slices. Two, 200 μm-thick spacers were placed across both ends of the 3 mm thick ceramic slices in each group. All those 3 mm slices with the spacers attached, were designated as the lower slices.

For each pair of ceramic slices, a silane-coupling agent[d], was applied to one surface of each slice according to the manufacturer's instructions. This product is packaged as two solutions, A and B (Table 1). One drop of each solution was mixed and applied with a sponge pellet to the polished ceramic surface which after 5 seconds, was gently air dried. Equal amounts of paste A and paste B of a dual-cure adhesive resin cement[e] were then mixed and applied to each of the silanated ceramic surfaces. The ceramic slices were then positioned together and a load of 35g was applied for 30 s. During this time, any excess cement around the periphery, was wiped away with a brush.

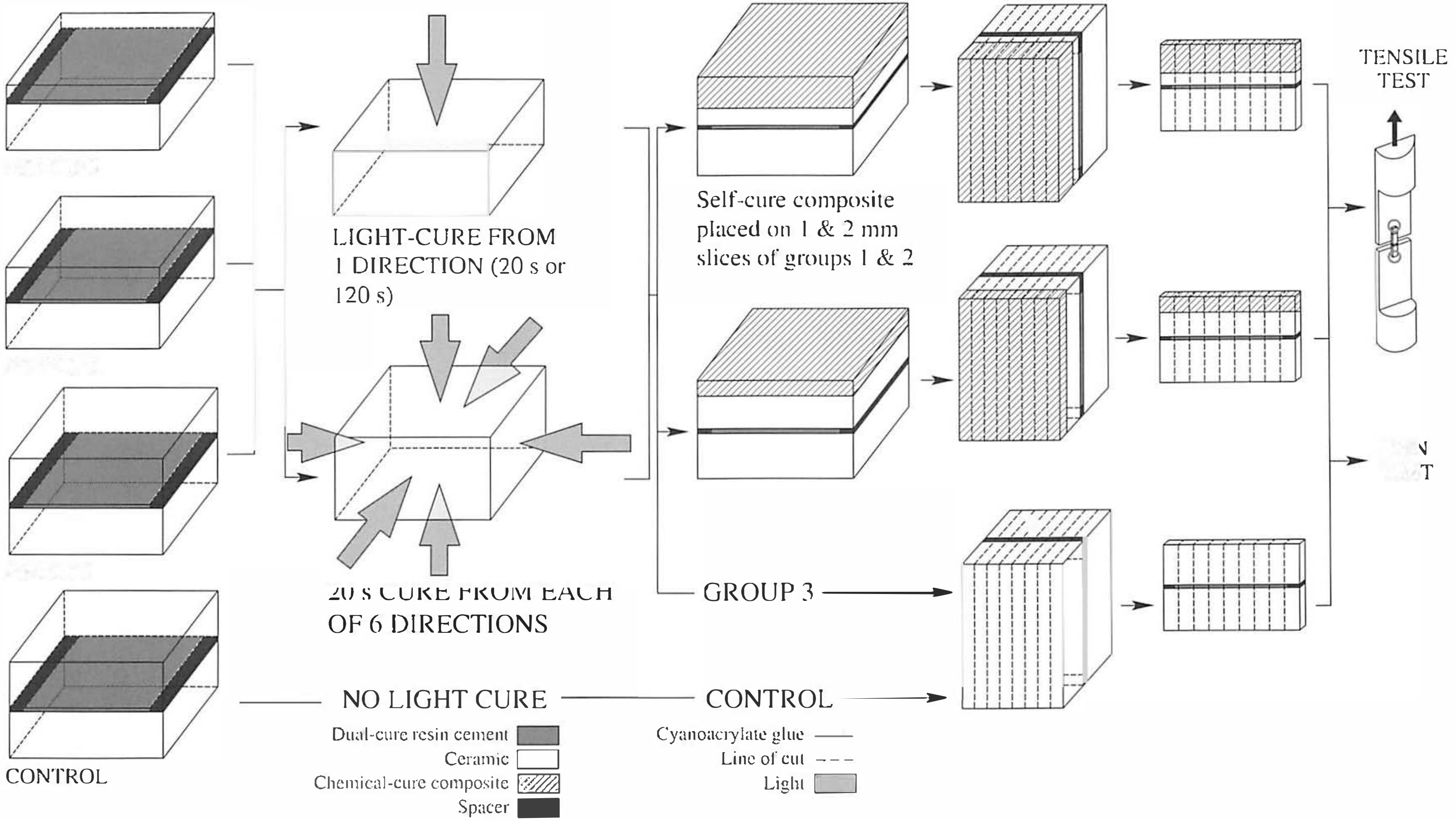
The bonded specimens of Groups 1, 2, and 3 were further divided into three sub-groups of two bonded specimens each (one bonded specimen for the microtensile bond strength test and the other for the microhardness test). Each sub-group was subjected to one of the following light-curing strategies: 20 s through the upper slice (one direction), 120 s through the upper slice, and 20 s from each of six directions, using a conventional light source[f]. The tip diameter of the light guide was 12.25mm. Prior to each bonding procedure, the power density of the light source was checked with a digital radiometer[g] to ensure a constant output. The mean (five readings) power density of the light source was 705 ± 4 mW/cm^2. The two pairs of bonded specimens in the Control group received no light-cure and were placed in darkness for 30 minutes. To ensure that the subsequent beams would have grips for attachment to the testing apparatus, chemical-cure composite[h], was added to the upper ceramic slices of Groups 1 and 2. This addition also ensured that the upper slices in all the groups had a total thickness of 3 mm.

All bonded specimens were stored in water at 37 °C. After 24 h, each specimen was attached to the arm of a low-speed diamond saw[i] and eight vertical cuts were made perpendicular to the bonded interface under water-cooling, to harvest slabs approximately 0.8 mm thick.

Microtensile bond strength evaluation

The two center slabs from each group were selected and bonded separately using cyanoacrylate glue[j] to glass microscope slides[k]. Another glass slide, bonded to a custom-molded acrylic base-plate which was slotted into the outer casing of the diamond saw, acted as a guide for the transverse slicing of the slabs into beams 6 mm in length and with a mean cross-sectional area of 0.60 ± 0.09 mm^2, measured using digital calipers[c]. Each slab yielded a maximum of 9 beams. Since the first and last beams were not included, as these were at the positions of the spacers, the maximum yield from the two slabs was 14 beams.
Using cyanoacrylate glue, each beam was carefully bonded onto a testing device[l] mounted in a universal testing machine[m], for the micro-tensile bond strength test. Each beam was then subjected to a tensile force at a crosshead speed of 1 mm/min. The values for the load at failure and surface area enabled calculation of μTBS in units of stress (MPa). For each group, 14 beams were sectioned for

Figure 1. Schematic illustration of specimen preparation for the microtensile and microhardness tests



testing to obtain means and standard deviations in μTBS.

Microhardness evaluation

The two center slabs from each group were selected and then wet-ground and polished using diamond pastes[n] down to 1 μm. Each polished slab was affixed horizontally using utility wax, polished side up, onto a glass microscope slide and positioned on the travelling micrometer stage of a micro- indentation tester[o] fitted with a diamond Knoop indenter. A load of 50 g was applied for a dwell period of 15 seconds. A series of five indentations were made horizontally along the center of the resin cement band of each slab, at 400 μm intervals. Using 400x magnification, the length of the long diagonal (μm) of each indentation was measured and the Knoop Hardness Number (KHN) calculated. A total of 10 indentations were made in each group to calculate the mean KHN.

Laser scanning confocal microscopy observation of specimen failure mode

Following bond strength testing, all fractured beams (240) were bonded[i] to strips of carbon tape, which were placed on brass tablets. Laser scanning confocal microscopy (LSCM)[p] was initially performed without any subsequent specimen preparation. However, to improve the clarity and contrast of the images, the de-bonded surfaces of the failed beams were gold-sputter coated[q] (300 Å thickness). LSCM is very convenient for determining the failure mode of debonded ceramic beams because an accurate 3-D image of the de-bonded surface, with no out-of focus blur can be quickly obtained by making and assembling a series optical tomograms (Van Meerbeek *et al,* 2000). In addition, no special preparation of the specimens such as dehydration in a vacuum, which may introduce artifacts, is required (Van Meerbeek *et al,* 2000). Failure mode was classified as: A, complete cohesive failure within ceramic; B, complete adhesive failure at the ceramic-resin cement interface; C, mixed adhesive/cohesive of the resin cement at the bonded interface; D, complete cohesive failure within the resin cement.

Statistical analysis

Two-way analysis of variance (ANOVA) with Fisher's least significant difference post-hoc test at a confidence of 95% ($p<0.05$), was used to determine any significant differences within the data from the microtensile bond strength and microhardness tests with respect to method of exposure direction and thickness of overlying ceramic.

Results

The mean microtensile bond strengths (μTBS), Knoop Hardness Values (KHN) and standard deviations are listed in Tables 2 and 3, respectively. Two-way ANOVA revealed that there was no statistically significant interaction between the type of photo-cure direction and ceramic thickness in the case of both μTBS and KHN ($p>0.05$). For each group, the μTBS and KHN of the ceramic slices exposed for 20 s from one direction were significantly lower than those exposed for 120 s from one direction and those exposed for 20 s from each of six directions ($p<0.05$). When exposed from one direction, the bond strength of Group 3 was significantly lower than that of Groups 1 and 2 respectively ($p<0.05$). However, there was no significant reduction in bond strength when the groups were exposed for 20 s from each of six directions ($p>0.05$). In particular, the μTBS of the Control Group, Group 3 exposed for 20 s from one direction, and Group 3 exposed for 120 s from one direction, 13 ± 9, 11 ± 10 and 16 ± 9

Table 1.
Materials, manufacturers, batch numbers and composition

Materials	Manufacturer	Batch No.	Composition
VITA CELAY BLANK	Vita Zahnfabrik, Bad Säckingen, Germany	128	Feldspathic porcelain
TOKUSO CERAMIC PRIMER (Solutions A and B)	Tokuyama Co., Tokyo, Japan	310228	Phosphoric acid monomer, Ethanol, γ-methacryloxypropyl- trimethoxysilane
Bistite II Resin Cement (Pastes A and B)	Tokuyama Co., Tokyo, Japan	A11028	Filler (77wt%) SiO_2-ZrO_2, Monomer(23et%) 2,2-bis[4-(2-methacryloxy) phenyl] propane, neopentyl glycol dimethacrylate, 11-methacryloxy-1,1-undecane, dicarboxylic acid (MAC-10), chemical and photoinitiators.

Table 2.
Mean tensile bond strengths, (MPa), of the groups *vs.* curing strategy

Light-curing strategy	GROUP 1 (1 mm)	GROUP 2 (2 mm)	GROUP 3 (3 mm)	CONTROL
No light	-	-	-	13 ± 9^{a}
1 direction (20s)	21 ± 9^{b}	20 ± 11^{b}	11 ± 10^{a}	-
1 direction (120s)	32 ± 5^{d}	32 ± 7^{d}	16 ± 9^{a}	-
6 directions	29 ± 6^{cd}	29 ± 9^{cd}	23 ± 7^{bc}	-

All values $x \pm SD$ ($n = 14$).
Values designated with the same superscript letters are not statistically different ($p>0.05$).

MPa, respectively, were significantly lower than those of the other groups ($p<0.05$). There were no significant differences between the bond strengths of Groups 1 and 2 when exposure was for 120 s from one direction, and for 20 s from each of six directions ($p>0.05$).

Out of a possible maximum of 140 beams, 3 beams from the Control Group and 4 beams from Group 3 exposed for 20 s from one direction, failed during final slicing prior to testing. The data of these specimens are included in the final results as zero bond strengths.

Regarding hardness values, the Control Group had the lowest KHN (70 ± 8), which was significantly lower than those of the light-cured groups ($p<0.05$).

Although the hardness of Groups 1 and 2 when exposed for 120 s from one direction were significantly higher than all the other groups ($p<0.05$) when the ceramic thickness was increased to 3 mm, a significant reduction in hardness occurred ($p<0.05$). However, when light was applied for 20 s from each of six directions, and the ceramic thickness increased from 2 to 3 mm, there was no reduction in hardness.

Laser scanning confocal microscopy observations of the modes of specimen failure, are presented in Table 4. Although one beam from Group 1 exposed for 20 s from each of six directions, exhibited complete cohesive failure in the ceramic, in all the groups, the mode of specimen failure was primarily a mixture of cohesive and adhesive failure of the resin cement at the bonded interface.

Discusssion

The present study found that when no light exposure was applied, the hardness of the control group was significantly lower than the irradiated groups. This result agrees with the findings of others (El-Mowafy *et al.,* 1999; El-Badrawy and El-Mowafy, 1995). When the duration of exposure was increased from 20 s to 120 s from one direction, significant increases in resin hardness occurred in

Table 3.
Mean microhardness, (KHN), of the groups *vs.* curing strategy

Light-curing strategy	GROUP 1 (1 mm)	GROUP 2 (2 mm)	GROUP 3 (3 mm)	CONTROL
None	-	-	-	70 ± 8^{f}
1 Direction (20s)	81 ± 5^{ad}	79 ± 5^{a}	78 ± 8^{a}	-
1 Direction (120s	113 ± 6^{e}	123 ± 7^{e}	86 ± 3^{d}	-
6 Directions	101 ± 4^{c}	92 ± 5^{b}	96 ± 5^{bc}	-

All values $x \pm$ SD ($n = 10$).
Values designated with the same superscript letters are not statistically different

Table 4.
Classification of failure mode

Failure Mode	**Control** (no light)	**Gp 1 (1mm)** 20s	120s	6 dir	**Gp 2 (2 mm)** 20s	120s	6-di	**Gp 3 (3 mm)** 20s	120s	6-dir
A	0	0	0	1	0	0	0	0	0	0
B	0	0	0	0	0	0	0	0	1	0
C	12	12	11	13	13	11	14	13	13	14
D	2	2	3	0	1	3	0	1	0	0

A: Complete cohesive failure within ceramic
B: Complete adhesive failure of the resin-cement at the bonded interface.
C: Mixed cohesive/adhesive failure of the resin-cement at the bonded interface.
D: Complete cohesive failure within resin cement.

each group. However, when the overlying ceramic thickness was increased from 2 to 3 mm, a significant reduction in hardness occurred, even when exposure was for 120 s from one direction. On the otherhand, when light was applied for 20 s from each of six directions, hardness did not decrease, which indicates that this exposure strategy was effective in increasing the hardness of the tested dual-cure resin cement. This increase in resin hardness probably resulted from the fact that when the light source was aimed at the sides of the bonded specimens, the cement layer sandwiched between the ceramic slices was directly exposed to light. Furthermore, the significant increase in hardness when light exposure was applied from one direction for only 20 s compared to the control group, indicates that even a small amount of light passing through the ceramic can significantly increase hardness of dual-cure resin cement. However, for the dual-cure resin cement system used in this study, 20 s exposure from one direction through ceramic is not sufficient to achieve maximum resin hardness. The hardness values in this study indicate the degree of cure of the resin matrix and while comparisons can be made within a single resin cement system, hardness values cannot be compared between or among other commercial products, because of differences in the composition and amount of the filler particles (Rueggeberg *et al.,* 2000).

The lowest μTBS was shown by the control group and Group 3, exposed for 20 s from one direction, which indicates that the bonding of dual-cure resin cement to ceramic may be poor when not enough light reaches the resin layer. The tensile bond strengths of both Groups 1 and 2 significantly increased, when the exposure time from one direction was lengthened from 20 to 120 s. These values were higher than those obtained when exposure was for 20 s from each of six directions. However, when overlying ceramic thickness was increased from 2 to 3 mm, bond strengths significantly reduced, when light exposure was from one direction. On the other hand, when exposure was for 20 s from each of six directions, there was a reduction in bond strength but this was not significant. The 1 and 2 mm thick ceramic slices used in this study represent a range of thickness for a porcelain veneer. The results of this experiment indicate that when a porcelain veneer is bonded using dual-cure resin cement, exposure to light from a conventional light source of similar power density to that used in this study for 20 s from one direction, is not long enough to obtain good bonding. Either the exposure duration should be lengthened or the light source should be directed at the veneer, from more than one direction to include all the margins. In the case of a ceramic onlay, if one or more cusps are to be replaced, ceramic thickness could exceed 2 mm. This could lead to regions of the resin layer being vulnerable to underexposure if not enough light passes through the ceramic. In the present study, when overlying ceramic thickness exceeded 2 mm, exposure from one direction, even for 120 s, was not sufficient to obtain optimum bond strengths. An exposure strategy of 20 s each from six directions ensured that all the exposed resin margins were exposed to light and resulted in an improvement in its mechanical properties and bond strength. This finding indicates that when a dual-cure resin cement-bonded ceramic onlay is exposed to light, as well as exposing through the occlusal surface, it is important to ensure that all the accessible margins of the restoration are exposed to light.

In the present study, the majority of the specimens failed at both the upper and lower ceramic interfaces, and the mode of failure was primarily a mixture of cohesive and adhesive failure of the resin cement at the bonded interface. However, these results differ from those of studies employing the conventional tensile bond test to evaluate the bonding of adhesive resin cements to ceramic materials (Kern and Thompson, 1995; O'Keefe *et al.,* 2000). These studies found that all the failures occurred cohesively within the resin cement (Kern and Thompson, 1995; O'Keefe *et al.,* 2000). O'Keefe *et al.*, 2000, in particular, evaluated the bonding of adhesive resin cements to zirconium oxide in conjunction with a silane coupling agent and found that the higher the bond strength, the higher the percentage of cohesive failure within the cement. Earlier generations of resin cements have relied on micromechanical retention created by sandblasting or etching with hydrofluoric acid, and organosilane coupling agents to bond to ceramic(Roulet and Degrange, 1996). However advances in polymer chemistry have lead to a new generation of multi-component liquid ceramic surface treatments that are capable of coupling resin cement strongly to ceramic without such treatments (Berry *et al.,* 1999; Barghi *et al.,* 2000). The two-liquid ceramic priming/dual-cure resin cement system used in the present study is representative of this new generation of resin cement-ceramic bonding systems. This system is also used for the intra-oral repair of a fractured ceramic restoration.

Whilst the thickness of dual-cure resin cement layer has been shown to influence tensile bond strength (Molin *et al.,* 1996), previous research demonstrated that the average marginal gap of Celay inlays may be up to 190 mm (Sjögren, 1995). In addition, Uno *et al.*, 2001, reported that after Cerec 2 inlays were cemented with dual-cure resin cement, the thickness of the cement layer was around 200 mm. In this study, a 200 mm cement thickness, in addition to corresponding to *in vitro* marginal gap widths for Celay inlays(Sjögren, 1995), also gave a sufficient width for the microhardness test to be performed. A 200 mm resin cement band width allowed for the fact that when polishing the slabs, due to differences in hardness, greater wear of the resin cement occurs at the bonded interfaces on either side of the cement band creating microscopic step defects which must be avoided when making the indentations. When resin cement film thickness is less than that used in this study, most of the specimens may be expected to de-bond at the adhesive interface because of the lack of defects such as air pockets. However, further research is needed to determine how the thickness of the dual-cure resin cement layer influences its' bonding to ceramic, particularly since it was reported that the regional marginal gap widths of a copy-milled restoration may vary(Sjögren, 1995).

The bond between dual-cure resin cement and ceramic may also be influenced by the shade of the ceramic material. Previous research demonstrated that the exposure time needed to optimally cure resin cement was affected by shade (Chan and Boyer, 1989). Exposure through shade C-4 porcelain needed to be increased, compared to that for shade B-2, and a greater hardness was achieved for a given thickness of the lighter shade than the darker shade. Since the ceramic specimens in present experiment were all of a relatively light-shade (A-2M), it is therefore possible that darker shades could give lower bond strengths. However, further research on the effect of ceramic shade on resin/ ceramic bond strength is necessary. Within the limitations of this *in-vitro* study, we conclude that the direction of light source application had no significant effect on either the microtensile bond strength or the hardness of the tested dual-cure resin cement when the thickness of overlying ceramic was 2.0 mm or less. When ceramic thickness was greater than this value, the use of multiple directed exposures demonstrated significantly better bond strength and hardness than a single exposure duration.

a. Vita Celay blank, Vita Zahnfabrik, Bäd Säckingen, Germany.
b. Leitz 1600 saw microtome, Ernst Leitz, Wetzlar, Germany
c. Mitutoyo CD15, Mitutoyo Co., Japan
d. Tokuso Ceramics Primer, Tokuyama Co., Tokyo, Japan
e. Bistite II dual-cure resin cement, Tokuyama Co., Tokyo, Japan
f. Tokuso Power Lite, serial no. 411521, Tokuyama Co., Tokyo, Japan
g. Jetlite light tester, serial no. 9061727, J.Morita USA inc., Mason Ivine, CA, USA
h. Clearfil FII, Kuraray Co. Ltd., Osaka, Japan
i Isomet, Buehler Ltd., Lake Bluff, IL, USA
j. Zapit, DVA, Anaheim, CA, USA
k. Microslide glass, Matsunami Glass Ind. Ltd., Japan
l. Bencor-Multi-T, Danville Engineering Co., San Ramon, USA
m. EZ-test, Shimadzu, Kyoto, Japan

n. DP-paste P, Struers A/S, Denmark
o. Akashi MVK-E hardness tester, Omron Takeisi Electronics Co.,
p. 1LM15W, Lasertec Co., Yokohama, Japan
q. Elionix Quick Auto Coater, Elionix Inc., Japan

Chapter 2

Durability of the dual-cure resin cement/ceramic bond with different curing strategies

Introduction

Recently, a new generation of multi-component liquid ceramic priming agents has been introduced for coupling resin cement or resin composite to ceramic (Matsumura *et al.,* 1997). These consist of two or three solutions, one of which contains a silane-coupling agent and the other an acidic phosphate monomer to catalyse the coupling reaction. Previous research has shown that this new generation of ceramic primers can strongly couple resin to fired porcelain and machined ceramic restorations without prior sandblasting or hydrofluoric acid-etching of the ceramic surface (Aida *et al.,* 1995; Barghi *et al.,* 2000; Berry *et al.,* 1999; Matsumura *et al.,* 1997).

Dual-cure resin cement is recommended for luting ceramic restorations because of its extended working time and controlled polymerization through the inclusion of both chemical initiators and photoinitiators (Cook and Standish, 1983; Krämer *et al.,* 2000). For dual-cure resin cement to possess good mechanical properties and bonding capability, a high degree of polymerization is necessary (Althoff *et al.,* 2000; Harashima *et al.,* 1991). This is achieved by applying light to activate the photoinitiators and start polymerization (Stansbury, 2000). However, previous research has demonstrated that both ceramic shade and thickness, and exposure duration affect the quantity of light reaching the resin-cement layer and may thus affect its mechanical properties (Blackman *et al.,* 1990; Chan and Boyer, 1989). In the absence of light, polymerization must start by chemical initiation, which results in the dual-cure resin cement having poorer mechanical properties (El-Badrawy and El-Mowafy, 1995;

El-Mowafy *et al.*, 1999) and bonding capability (Foxton *et al.*, in press). Therefore, it is recommended to direct the light curing tip at aceramic restoration from several directions, to ensure that as much light as possible reaches the resin cement layer (Goldstein, 1998; Thordrup *et al.*, 1999).

The microtensile bond strength (μTBS) test offers several advantages over conventional shear and tensile bond strength tests for evaluating the durability of the dual-cure resin cement/ceramic bond (Sano *et al.*, 1994; Shono *et al.*, 1999; Shono *et al.*, 1999). When the μTBS test is employed, the direction of the curing light can be precisely controlled and multiple serial slabs, less than 1 mm thick, can be harvested from one specimen, stored in water, and evaluated at different intervals over a period of time. When employing water storage as a parameter for determining the durability of the resin/ceramic bond, it is important that the resin is saturated with water in order to test the water stability of adhesive bonding (Kern and Thompson, 1995). The length of time required for complete saturation will depend on the dimensions of the stored specimen. The smaller the stored specimen, the greater the ratio of water saturated resin cement to unsaturated resin cement, and thus the time required to obtain 100% water saturation of the resin cement is less. Therefore, the μTBS test also offers the possibility of reduced water storage times compared to those required for conventional shear and tensile bond strength tests for evaluating bond stability.

Information on the durability of the bond between dual-cure resin cement and machine-milled ceramic treated with a multi-component ceramic primer is limited. Kamada et al., 1998, found that after thermal cycling specimens of machinable ceramic treated with a multi-component ceramic primer and bonded using dual-cure and chemical-cure resin cements, there were no significant reductions in shear bond strength. However, there is no information available on what effects chemical-cure alone and irradiating from one or multiple directions have on the stability of the bond between dual-cure resin cement and machinable ceramic when stored in water.

The purpose of this study was to evaluate the effects of chemical-cure, exposure to light from one direction, and exposure to light from multiple directions, on the stability in water of the bond between dual-cure resin cement and a machinable ceramic treated with a multi-component ceramic primer. Two dual-cure resin cements and two multi-component ceramic primers were tested. Since the manufacturers suggest using their own dual-cure resin cements with their ceramic primers, two homogeneous and two heterogeneous combinations of primer and cement were tested. The null hypothesis was that the mode of polymerization initiation does not affect stability in water, the bond between ceramic treated with a multi-component ceramic primer and dual-cure resin cement.

Materials and Methods

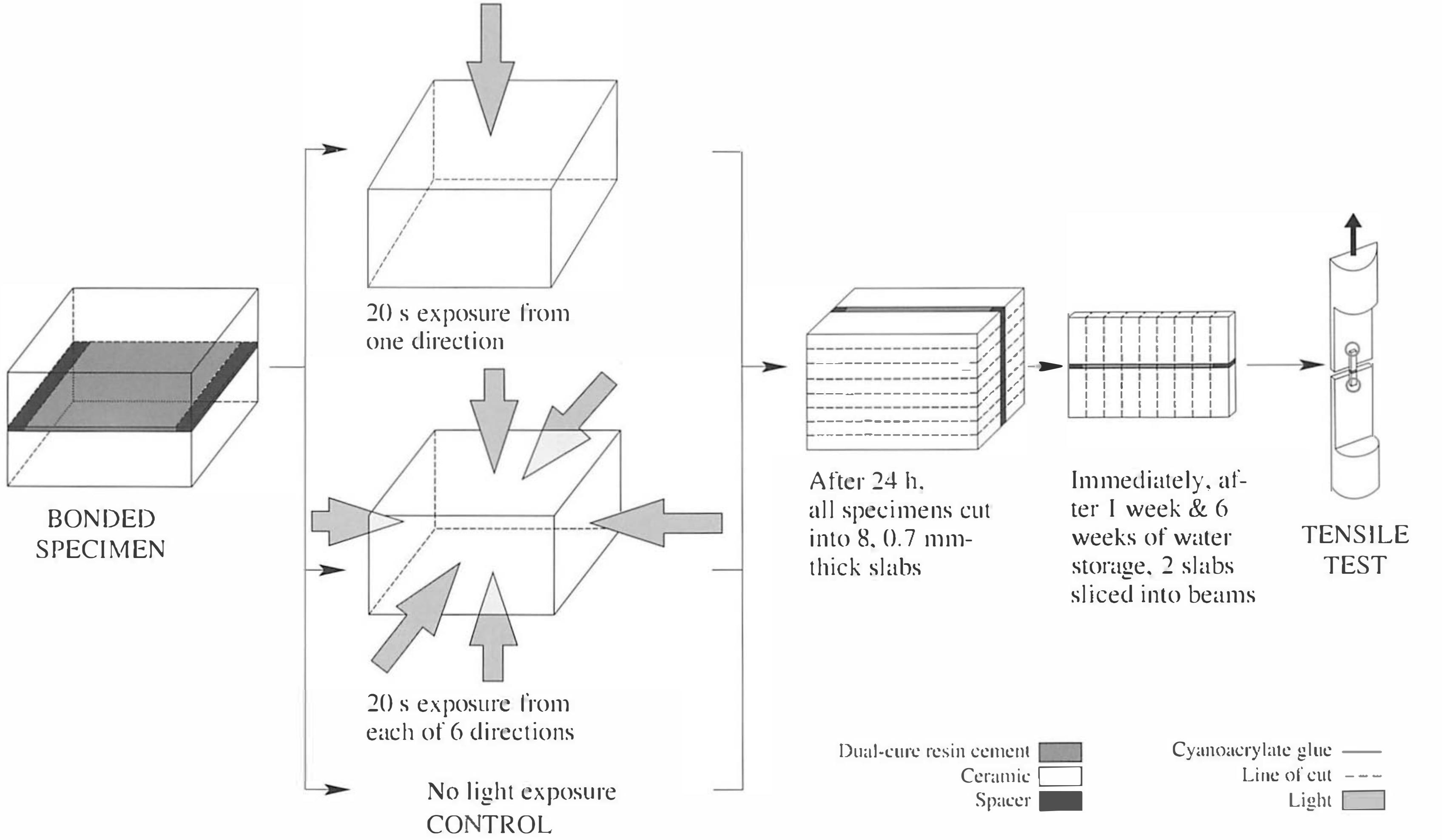
Specimen Preparation

Ceramic blocks, shade A2M, were cut using a horizontal diamond cutting saw(Leitz 1600 saw microtome, Ernst Leitz, Wetzlar, Germany) under running water, into 24 slices measuring 12 x 10 x 3 mm thick. The surfaces of each ceramic slice were carefully polished using wet 600-grit silicon carbide paper, then cleaned in an ultrasonic water bath for five minutes. After polishing, ceramic thickness was measured with digital calipers (Mitutoyo CD15, Mitutoyo Co., Japan) to ensure that their thicknesses were accurate to within 0.1 mm. The materials used in this study are shown in Table 1.

Bonding Procedure

Pairs of ceramic slices were randomly divided into four experimental groups as described in Table 2. Two 200 μm-thick spacers were placed across

Figure 1. Schematic illustration of specimen preparation for microtensile tests



both ends of one slice in each of the four groups, which were then bonded as follows: (1) surface treatment with Tokuso Ceramic Primer (TCP), and bonded using Bistite II (TCP/BisII), (2) surface treatment with K-Etchant gel and then with Clearfil Liner Bond 2V Primer (LB2V Primer) and Porcelain Bond Activator (PBA), and bonded using Bistite II (LB2V/BisII), (3) surface treatment with TCP and bonded using Panavia F (TCP/PanF) and (4) surface treatment with K-etchant gel, then with LB2V Primer and PBA, and bonded using Panavia F, (LB2V/PanF). All bonding procedures were carried out according to the manufacturers' instructions. The ceramic slices were carefully positioned together and a load of 35 g was applied on the upper slice while the excess cement was wiped away with a brush to ensure even film thickness.

Each group was further divided into three sub-groups according to the curing strategy: (1) application of an air-inhibiting agent on the exposed resin cement borders (Oxygard II, Kuraray Co., Osaka, Japan) and placement in darkness for 30 minutes at room temperature (No light, Controls), (2) exposure to light for 20 s from one direction (the exposure time recommended by the manufacturers) (1 direction), and (3) exposure for 20 s from each of six different directions (6 directions). A conventional light source (Tokuso Powerlite, Tokuyama Co., Tokyo) with a tip diameter of 12.25 mm was used. Prior to each bonding procedure, the power density of the light source was checked with a digital radiometer (Jetlite light tester, J. Morita USA inc., Mason Irvine, CA, USA) to ensure a similar output. The mean power density of the light source was 705±4 mW/cm^2. All the bonded specimens were then stored in water at 37 °C for 24 hours.

Bond Strength Testing

After 24 h, each bonded specimen was attached to the arm of a low-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) and nine

Table 1. Materials used in this study

Material	Manufacturer	Batch number	Composition
Vita Celay Blank	Vita Zahnfabrik H Rauter GmbH & Co.KG Bäd Sackingen, Germany	05BY0139	Feldspathic porcelain
Tokuso Ceramic Primer (TCP) (A + B)	Tokuyama Co., Tokyo, Japan	31028	Phosphate monomer, γ-methacyloxypropyl trimethoxysilane, ethanol
Bistite II (A + B) (BisII)	Tokuyama Co., Tokyo, Japan	A12450	Filler (77%), Bis-GMA, MAC-10, chemical initiators, photoinitiators
K-etchant gel	Kuraray Co., Osaka, Japan	-	40% H_3PO_4
Clearfil Liner Bond 2V Primer (A + B) (LB2V)	Kuraray Co., Osaka, Japan	011130	MDP, HEMA, H_2O, chemical initiators, photoinitiators
Porcelain Bond Activator (PBA)	Kuraray Co., Osaka, Japan	0087A	γ- methacyloxypropyl trimethoxysilane, monomers
Panavia F (A + B) (PanF)	Kuraray Co., Osaka, Japan	011182	Filler (78%), MDP, dimethacrylates, chemical and photoinitiators.

Table 2. Experimental groups and bonding procedures

Group	Etchant	Ceramic Primer	Dual-cure resin cement	Procedures*
TCP / BisII	None	Tokuso Ceramic Primer	Bistite II	b; c; d; e; f
LB2V/ BisII	K-etchant	Clearfil Liner Bond 2V Primer / Porcelain Bond Activator	Bistite II	a; b; c; d; e; f
TCP / PanF	None	Tokuso Ceramic Primer	Panavia F	b; c; d; e; f
LB2V / PanF	K-etchant	Clearfil Liner Bond 2V Primer / Porcelain Bond Activator	Panavia F	a; b; c; d; e; f

*Procedures: a = apply H_3PO_4 gel for 10 s, then rinse; b = mix one drop of each solution together and apply for 30 s, then gently air dry for 10 s;
c = mix equal amounts of resin cement and apply; d = no-light cure;
e = expose to light for 20 s from one direction; f = expose to light for 20 s from each of six directions.

vertical cuts were made perpendicular to the bonded interface under water - cooling, to harvest slabs approximately 0.7 mm thick, as depicted in Figure 1. Immediately, after one week and after six weeks of storage in water , which was changed every day until testing, two slabs were randomly selected from each sub-group and bonded separately using cyanoacrylate glue (Zapit, DVA, Anaheim, CA, USA) to glass microscope slides (Microslide glass, Matsunami Glass Ind. Ltd., Japan). Another glass slide, bonded to a custom-molded acrylic base-plate which was slotted into the outer casing of the diamond saw, acted as a guide for the transverse slicing of the slabs into beams 6 mm in length and with a mean cross-sectional area of 0.54 ± 0.08 mm^2, measured using digital calipers. Each slab yielded a maximum of nine beams, however, since the first and last beams could not be included as these were at the positions of the spacers, the yield from one slab equaled 7 beams. Thus, in each sub-group, the maximum number of beams that could be harvested for testing was 14.

Using cyanoacrylate glue, each beam was carefully bonded onto a testing device (Bencor-Multi-T, Danville Engineering Co., San Ramon, USA) mounted in a table top material tester (EZ-Test, Shimadzu Co., Kyoto, Japan), and subjected to a tensile force at a crosshead speed of 1 mm/min. The values for the load at failure and surface area enabled calculation of mTBS in units of stress (MPa).

Laser scanning confocal microscopy

The laser scanning confocal microscope is very convenient for determining the failure mode of debonded ceramic beams because an accurate 3-D image of the de-bonded surface, with no out-of focus blur can be quickly obtained by making and assembling a series of optical tomograms (Van Meerbeek, 2000). Following bond strength testing, all the failed beams (504) were bonded to brass tablets. Laser scanning confocal microscopy (LSCM)(1LM15W, Lasertec Co., Yokohama, Japan), was initially performed without any subsequent specimen preparation. However, to improve the clarity and contrast of the images, the de-bonded surfaces of the failed beams were gold-sputter coated (Elionix Quick Auto Coater, Elionix, Japan). A transparent grid divided into squares measuring 6 mm x 6 mm (25 % of the bar length) was used to map the percentage of ceramic/resin-cement visible on enlarged micrographs of all the de-bonded surfaces.

Failure mode was classified as: A, 100 % adhesive failure at the bonded interface; B, more than 50% adhesive failure of the resin cement at the bonded interface; C, less than 50% adhesive failure of the resin cement at the bonded interface; D, cohesive failure within resin cement; and E, cohesive failure within ceramic.

Statistics

Nonparametric statistical tests were employed since the data were not normally distributed and there were inequalities in the variances. The microtensile bond strength data were analyzed using the Kruskal-Wallis rank test and subjected to multiple paired comparisons using the Wilcoxon signed rank sum test. Statistical significance was considered as $P<0.05$. The effects of the four factors, cement, primer, curing strategy and storage time on tensile bond strength were tested using the Mann-Whitney U test for resin cement and ceramic primer, and the Kruskal-Wallis rank test for curing strategy and storage time. Statistical analysis of the failure modes was performed using the Kruskal-Wallis rank test. For this, each failure mode was given a score from 1 to 5 prior to statistical analysis (Matsumura *et al.,* 1997). A score of 1 was given for 100 % adhesive failure at the bonded interface, a score of 2 for more than 50% adhesive failure of the resin cement at the bonded interface, 3 for less than 50% adhesive failure of the resin cement at the bonded interface, 4 for cohesive failure within resin cement; and 5 for cohesive failure within ceramic. The higher the score, the stronger was the bond[17].

Results

The results of the Mann-Whitney U test and Kruskal-Wallis rank test revealed that the factors, resin cement, primer and curing strategy had significant effects on bond strength, $p<0.003$, $p<0.001$ and $p<0.001$, respectively. Storage time did not have a significant effect on bond strength ($P=0.3520$). Panavia F ranked higher than Bistite II, TCP higher than LB2V, and exposure to light from six directions higher than exposure to light from one direction and chemical cure.

The microtensile bond strengths are presented in Tables 3 and 4. Out of a maximum total of 504 beams, 85 failed during preparation for bond strength testing, and these are included in the results as zero bond strengths. After 1 day, the μTBS of the TCP/BisII and TCP/PanF groups cured chemically were significantly lower than those for the TCP/BisII and TCP/PanF groups exposed for 20s from each of six directions ($p<0.05$). In contrast, there were no significant differences in μTBS among the LB2V/BisII and LB2V/PanF sub-groups cured chemically and the LB2V/BisII and LB2V/PanF sub-groups exposed to light from six directions after 1 day ($p>0.05$).

Between 1 day and six weeks of water storage, the chemically cured TCP/BisII, LB2V/Bis II and LB2V/PanF sub-groups, all significantly decreased in μTBS ($p<0.05$), whereas chemical-cured TCP/PanF significantly increased in μTBS ($p<0.05$). After six weeks, there were no significant differences in μTBS between chemically cured TCP/PanF and both irradiated TCP/PanF sub-groups ($p>0.05$), which also increased in μTBS, but not significantly ($p>0.05$). However, both irradiated LB2V/PanF sub-groups significantly decreased in μTBS over time ($p<0.05$). On the other hand, both irradiated TCP/BisII sub-groups significantly increased in μTBS between 1 day and 6 weeks of water storage ($p<0.05$), and exposure for 20 s from each of six directions resulted in significantly higher μTBS than exposure for 20 s from one direction after both 1 day and six weeks of water storage ($p<0.05$). The μTBS of the irradiated LB2V/ BisII sub-groups were stable over the six-week period, however their values were lower than those of the irradiated TCP/BisII sub-groups. There was no significant difference between the μTBS of the LB2V/BisII groups exposed for 20 s from one direction and 20 s from each of six directions after 6 weeks of water storage ($p>0.05$).

The mean ranks of all the experimental sub-groups based on their modes of failure are presented in Table 5. The sub-groups with the highest mean rank had the highest bond strengths and those sub-groups with the lowest mean rank, the lowest bond strength. The changes in failure mode of each of the sub-groups over the six-week observation period are shown in Fig. 2. After 1 day of water storage, the predominant failure mode within the four main groups was a mixture of adhesive and cohesive failure of the resin cement at the ceramic interface. However, after 6 weeks of water storage, both irradiated TCP/BisII groups exhibited a greater percentage of cohesive failures in resin cement, whereas chemical-cured TCP/BisII exhibited an increase in the percentage of 100% adhesive failures. After six weeks, the LB2V/BisII sub-groups, cured chemically and exposed for 20 s from one direction, exhibited more, greater than 50% adhesive failures at the bonded interface and had lower mean ranks, than the sub-group cured for 20 s from six directions. In contrast almost all the beams of LB2V/Pan F sub-groups failed 100% adhesively at the ceramic interface whether polymerization was chemically or light initiated after six weeks water storage. These sub-groups had the lowest mean ranks. On the other hand, all the beams of the chemical-cured and irradiated TCP/PanF sub-groups failed cohesively within resin cement after six weeks. These sub-groups were ranked

Table 3.
Tensile bond strength (MPa) of the groups bonded using Bistite II

GROUP	EXPOSURE	1 DAY	1 WEEK	6 WEEKS
TCP/BisII	No Light	13.5 ± 8.6^{a}	11.1 ± 8.6^{ab}	3.8 ± 10.1^{b}
	1 Direction	11.4 ± 10.3^{ab}	19.7 ± 11.5^{e}	26.9 ± 9.6^{f}
	6 Directions	23.0 ± 7.1^{efg}	24.4 ± 6.6^{efg}	38.7 ± 7.5^{i}
LB2V/BisII	No Light	27.8 ± 11.6	21.4 ± 7.9^{B}	9.3 ± 8.5^{C}
	1 Direction	17.9 ± 17.7^{ABD}	19.5 ± 9.7^{ABDE}	18.4 ± 6.2^{DEF}
	6 Directions	24.5 ± 12.2^{ABDEFG}	24.1 ± 6.8^{ABDEFG}	21.9 ± 6.5^{BDEFG}

All values are mean ± SD
Groups with the same case superscript letters are not significantly different ($p>0.05$).

Table 4.
Tensile bond strength (MPa) of the groups bonded using Panavia F

GROUP	EXPOSURE	1 DAY	1 WEEK	6 WEEKS
TCP/PanF	No Light	23.1 ± 16.7^{a}	27.0 ± 7.2^{ab}	33.8 ± 6.6^{c}
	1 Direction	30.2 ± 9.4^{abcd}	35.8 ± 10.6^{cde}	39.4 ± 6.2^{cef}
	6 Directions	35.9 ± 10.2^{cdefg}	38.4 ± 7.6^{cdefgh}	40.3 ± 8.9^{cefgh}
LB2V/PanF	No Light	20.6 ± 12.0^{A}	0.3 ± 11.1^{B}	0^{B}
	1 Direction	14.3 ± 9.7^{D}	15.3 ± 11.5^{D}	2.9 ± 7.4^{BCF}
	6 Directions	24.4 ± 6.5^{AG}	25.5 ± 8.5^{AG}	3.9 ± 7.1^{CF}

All values are mean ± SD
Groups with the same case superscript letters are not significantly different ($p>0.05$)

Table 5.

Failure modes after microtensile bond test and Kruskal-Wallis mean rank

		No. of specimens for each failure mode (failure mode/score)					Kruskal-Wallis Mean Rank	
Sub-group-storage time		A/1	B/2	C/3	D/4	E/5		
TCP/PanF	NoL-6 wk	0	0	0	14	0	1	456.5
TCP/PanF	1 Dir-6 wk	0	0	0	14	0	1	456.5
TCP/PanF	6 Dir-6 wk	0	0	0	14	0	1	456.5
TCP/BisII	6 Dir-6 wk	0	0	4	10	0	4	415.5
TCP/BisII	6 Dir-1 dy	0	0	7	7	0	5	384.7
TCP/BisII	6 Dir-1 wk	0	0	7	7	0	6	384.7
LB2V/PanF	1 Dir-1 dy	0	2	6	6	0	7	349.9
LB2V/BisII	NoL-1 wk	0	0	14	0	0	8	313.0
TCP/BisII	1 Dir-1 dy	0	0	14	0	0	8	313.0
LB2V/BisII	1 Dir-1 wk	0	0	14	0	0	8	313.0
LB2V/PanF	6 Dir-1 dy	0	4	6	4	0	11	304.8
TCP/PanF	6 Dir-1 wk	0	5	5	4	0	12	302.8
TCP/PanF	6 Dir-1 dy	0	5	4	4	0	13	292.6
TCP/PanF	NoL -1 wk	0	2	12	0	0	14	288.4
LB2V/PanF	NoL-1 dy	0	2	12	0	0	14	288.4
TCP/PanF	NoL -1 dy	0	6	4	4	0	16	280.2
LB2V/BisII	6 Dir-6 wk	0	3	11	0	0	17	276.1
TCP/PanF	1 Dir-1 wk	0	3	11	0	0	17	276.1
LB2V/BisII	1 Dir-1 dy	0	5	7	2	0	19	272.1
LB2V/PanF	6 Dir-1 wk	0	5	9	0	0	20	251.6
LB2V/PanF	1 Dir-1 wk	0	6	8	0	0	21	239.3
LB2V/BisII	6 Dir-1 dy	2	4	7	0	1	22	237.5
LB2V/BisII	NoL-6 wk	0	7	7	0	0	23	227.0
LB2V/BisII	1 Dir-6 wk	0	7	7	0	0	23	227.0
TCP/BisII	1 Dir-6 wk	0	10	1	3	0	25	220.9
TCP/BisII	1 Dir-1 wk	0	10	4	0	0	26	190.1
TCP/PanF	1 Dir-1 dy	0	10	4	0	0	26	190.1
LB2V/BisII	6 Dir-1 wk	0	11	3	0	0	28	177.8
TCP/BisII	NoL-1 dy	0	13	1	0	0	29	153.3
LB2V/BisII	NoL-1 dy	0	14	0	0	0	30	141.0
TCP/BisII	NoL-1 wk	3	10	1	0	0	31	130.1
TCP/BisII	NoL-6 wk	7	7	0	0	0	32	93.0
LB2V/PanF	6 Dir-6wk	11	3	0	0	0	33	87.0
LB2V/PanF	NoL-1 wk	14	0	0	0	0	34	33.0
LB2V/PanF	NoL-6 wk	14	0	0	0	0	34	33.0
LB2V/PanF	1Dir-6 wk	14	0	0	0	0	34	33.0

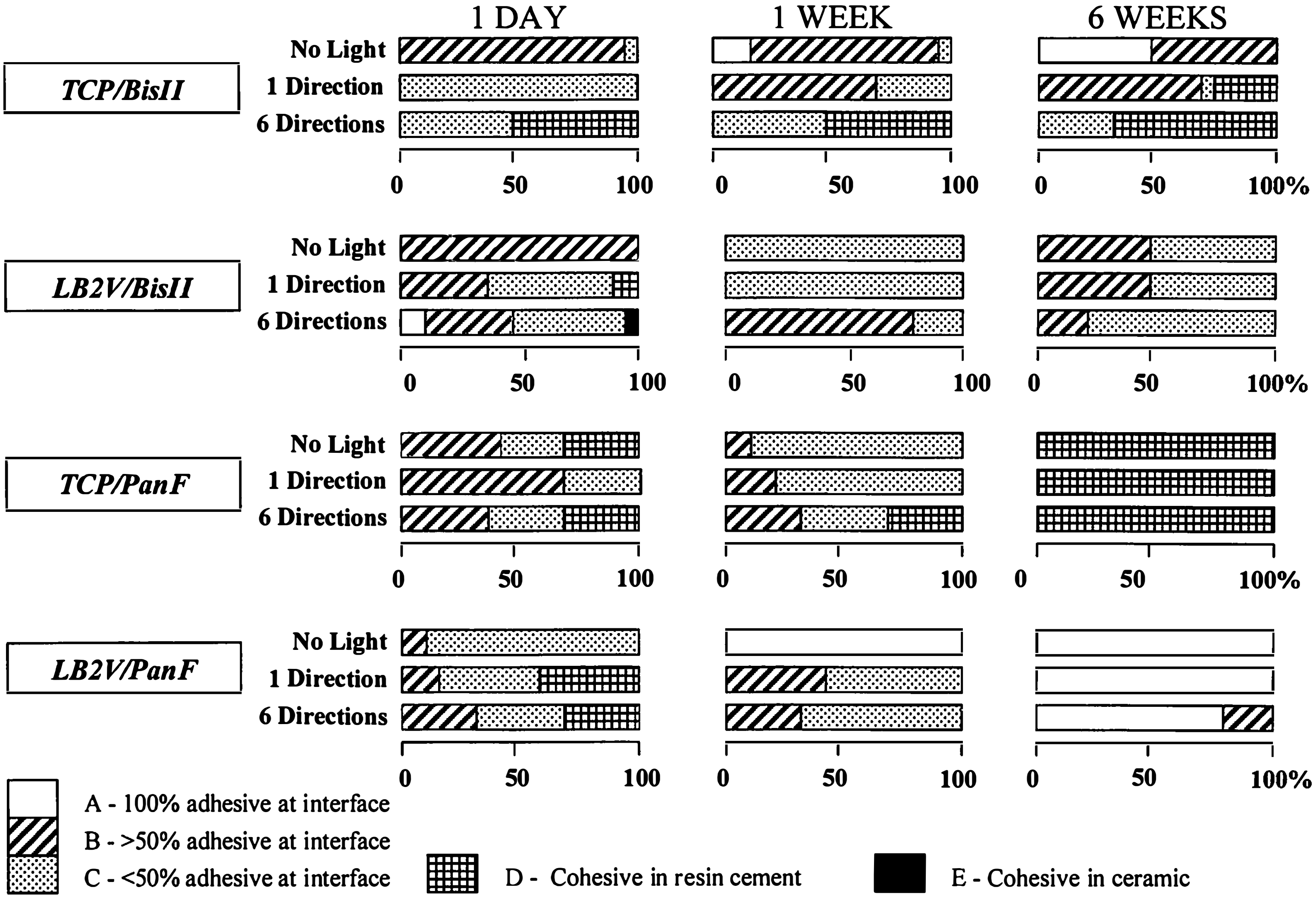


Figure 2. Classification of specimen failure mode

the highest.

Discussion

Previous *in-vitro* studies on the durability of the bond between dual-cure resin cement and ceramic treated with a multi-component ceramic primer have evaluated the effect of different ceramic surface treatments (Kamada *et al.,* 1998; Kato *et al.,* 1996; Matsumura *et al.,* 1997). However, the effects of different curing strategies on bond stability have received less attention. In particular, the effects of chemical versus light-activated polymerization on the durability of the dual-cure resin cement/ceramic bond, after long-term water storage.

In the present study, the durability of the bond between dual-cure resin cement and ceramic was dependent upon the curing strategy, ceramic primer and resin cement. These results suggest that there is a complex interaction between the multi-component ceramic primer, the dual-cure resin cement and the degree of polymerization, which affects the durability of the dual-cure resin cement/ceramic bond.

The two, multi-component ceramic primers used in the present study, have different chemical compositions. LB2V Primer is a self-etching dentin primer, whose chemical components include chemical initiators, photoinitiators, water, the hydrophilic monomer, HEMA and the phosphate monomer, MDP (Okada *et al.,* 1998). When PBA, which contains the silane coupling agent, γ-methacyloxypropyl trimethoxysilane (γ-MPS), is mixed with LB2V Primer, the alkoxy groups of γ-MPS are hydrolyzed into silanol groups and then activated by acid catalytic action with the MDP contained in the primer. When this mixture is applied to the ceramic surface, the activated γ-MPS reacts with the silanol groups on the ceramic surface (Okada *et al.,* 1998). We speculate that the high bond strengths of the chemical cured LB2V/BisII and LB2V/PanF sub-groups after 1 day of water storage were probably the result of chemical initiators in LB2V Primer initiating polymerization of the resin cement adjacent to the ceramic surface. However, after applying the mixture of LB2V Primer and PBA to the ceramic surface and air-drying, some residual water and HEMA will still be present on the ceramic surface when the resin cement is applied since the solvent of LB2V Primer is a water based solvent. Therefore it is speculated that residual H_2O and HEMA molecules may have interfered with siloxane bond formation and rendered the resin-cement/ceramic bond in the LB2V groups susceptible to hydrolytic degradation after long-term storage water (Roulet, 1998). TCP on the other hand, contains no chemical initiators and the solvent is ethanol. In the present experiment, the durability of the TCP/BisII sub-groups significantly improved when exposed to light. This result, together with the fact that no chemical initiators are present in TCP, indicates that the improved durability of the TCP/ BisII group was due to exposure to light. Ethanol quickly evaporates after being applied to a ceramic surface. Evaporation of the solvent may have enabled a higher number of siloxane bonds to form at the ceramic surface, thus rendering the resin cement/ceramic bond more resistant to hydrolytic degradation when immersed in water for a long period of time. Consequently, the μTBS of the TCP/BisII and TCP/PanF sub-groups were probably more dependent upon the polymerization kinetics of the two dual-cure resin cements than the LB2V/BisII and LB2V/PanF sub-groups were. Previous research has shown that chemically initiated polymerization does not enable dual-cure resin cement to develop optimum mechanical properties (El-Badrawy and El-Mowafy, 1995; El-Mowafy *et al.*, 1999). Our previous study, using Bistite II dual-cure resin cement, found that and when the ceramic is more than 2 mm thick, exposure for 20 s from each of six directions is significantly more effective for developing good mechanical properties and bonding capability than no exposure or 20 s exposure from one direction (Foxton *et al.*, in press). The present study used ceramic specimens, 3 mm thick, and when the ceramic was primed with TCP, chemical-cured TCP/BisII significantly decreased in µTBS over time whereas light-cured TCP/BisII significantly increased in µTBS over time. These results indicate that the durability of Bistite II dual-cure cement is dependent upon the curing strategy employed. Whereas, in the case of Panavia F, the µTBS of the chemically cured TCP/PanF sub-group significantly increased over time, such that after six weeks, there were no significant differences between the chemical and irradiated TCP/PanF sub-groups. This indicates that in the absence of light, the durability of Panavia F is dependent upon the multi-component ceramic primer. The mechanical properties of Bistite II may be higher when polymerization is light-activated as opposed to chemically-activated, whereas those of Panavia F are similar, whether polymerization is light or chemically activated (Foxton *et al.*, in press). The durability of the resin cement/ceramic bond can be evaluated *in-vitro* by thermal cycling and/or long-term water storage (Kamada *et al.,* 1998; Kato *et al.,* 1996; Matsumura *et al.*, 1997; Roulet *et al.,* 1995). Thermal cycling utilizes differences in the thermal coefficients of expansion of the substrate and the bonding material to stress the adhesive bond, whereas long-term water storage evaluates the resistance of the adhesive bond to hydrolytic degradation. Recently, Shono *et al.,* 1999, demonstrated that dividing large specimens into many small beams accelerated the deterioration of the resin-dentin bond in water. In addition, Okuda *et al.,* 2001, reported that when 0.7 mm thick slabs were stored in water, resin-dentin bond strengths decreased over time. When carrying out bond strength tests, adhesive failure of the resin cement/ceramic bond rather than cohesive failure of the ceramic substrate is preferable in order to evaluate the strength of the bond at the adhesive interface (Sano *et al.,* 1994). The µTBS test has been shown to give greater numbers of adhesive failures than conventional shear or tensile bond strength tests (Sano *et al.,* 1994). This result was attributed to the cross-sectional areas of the tested specimens, which were typically 1 mm^2 or less. Uno et al., 2000, bonded Cerec 2 ceramic to dentin using different dual-cure resin cements and after subjecting the specimens to the microtensile bond strength test, found that the specimens failed at either the inlay/ resin, resin/dentin interfaces or cohesively in the resin cement in almost equal numbers. In the present study, the 0.7 mm-thick slabs had a ratio of exposed resin cement to unexposed resin cement higher than that of the original bonded specimen (12 x 10 x 6 mm), thus reducing the time required for complete saturation of the resin cement layer and accelerating hydrolytic degradation of the adhesive bond. Although the period of water storage in the present study was six weeks, which is a relatively short time, reductions in bond strength were observed for the ceramic specimens, treated with phosphoric acid and LB2V Primer/ PBA. These were accompanied by an increase in the number of 100 % adhesive failure modes, indicating complete hydrolization of the siloxane bonds between the resin cement and the ceramic surface (Roulet, 1987). Therefore, for this particular ceramic priming system, six weeks of water storage was long enough for saturation of the adhesive bond.

In conclusion, the null hypothesis that the mode of polymerization initiation does not affect the durability of the bond between machinable ceramic treated with a multi-component ceramic primer and dual-cure resin cement in water must be rejected. The present study found that bond durability depended upon the amount of light received by the specimens, the dual-cure resin cement and the multi-component ceramic primer used. The tested dual-cure resin cements differed in their ability to polymerize chemically and in the amount of light required for photo-initiated polymerization, which influenced the durability of the dual-cure resin cement/ceramic bond. In addition, the resistance of the resin cement/ceramic bond to hydrolytic degradation appears to be dependent upon the chemical composition of the ceramic primer. The more hydrophilic is the ceramic primer, the poorer the stability of the dual-cure resin cement/ceramic bond.

Chapter 3

Long term durability of the dual-cure resin cement/silicon oxide ceramic bond

Introduction

Advances in polymer chemistry have lead to the development of a new generation of multi-component liquid ceramic surface treatments for coupling resin cement or composite resin to ceramic (Matsumura *et al.,* 1997). There are several types of multi-component liquid ceramic surface treatments such as, ceramic primers formulated to prime ceramic only, ceramic primers that are self-etching dentin priming systems combined with a separate silane coupling agent, and ceramic bonding agents which are adhesive dentin bonding agents combined with a separate silane coupling agent. They generally consist of two or three solvents, one of which contains a silane coupling agent, usually γ-methacyloxylpropyl-trimethoxysilane (γ-MPS), and the other, an acidic monomer to catalyse the coupling reaction. The solvent is usually either water or an organic solvent such as ethanol, and may also contain the hydrophilic monomer, HEMA. Previous research has shown that this new generation of multi-component liquid ceramic surface treatments can strongly couple resin to fired porcelain and machinable ceramic without prior sandblasting or hydrofluoric acid etching of the ceramic surface (Aida *et al.,* 1995; Barghi *et al.,* 2000; Berry *et al.,* 1999; Matsumura *et al.,* 1997; Sato *et al.,* 1999).

The long-term durability of the bond between resin and ceramic is of crucial importance for the longevity of bonded ceramic restorations. The resin-ceramic bond is, however, susceptible to hydrolytic degradation in the presence of water (Roulet, 1987). Hydrolytic degradation of the resin-ceramic bond may lead to de-bonding of the ceramic restoration (Roulet *et al.*, 1995). Resin-ceramic bond durability is evaluated in-vitro by thermal cycling and immersion in water. Thermal cycling utilizes differences in the thermal coefficients of expansion of the substrate and the bonding material to stress the adhesive bond, whereas water storage evaluates the resistance of the adhesive bond to hydrolytic degradation. A limited number of thermal cycling and water storage studies have been carried out on the durability of the bond between resin cement and ceramic treated with a multi-component ceramic surface treatment (Kamada *et al.*, 1998; Kamada *et al.*, 2001; Kato *et al.*, 1996; Matsumura *et al.*, 1997). Kato et al., 1996, concluded after thermal cycling ceramic specimens bonded with homogeneous luting systems, that the durability of the bond was influenced by the combination of silane primer and luting agent. Berry et al., 1999, reported that after storing tubes of dual-cure resin cement bonded to silanated porcelain for three months in water at room temperature, bond strengths remained either stable or increased, and all the failures were cohesive in porcelain.

When carrying out water storage studies, it is important that the resin is saturated with water in order to test the water stability of adhesive bonding (Kern *et al.*, 1995). The length of time required for complete saturation will depend on the dimensions of the stored specimen. The smaller the specimen, the greater the ratio of exposed resin cement to unexposed resin cement, and thus the time required to obtain 100% water saturation of the resin cement is less. Shono et al., 1999, reported that dividing large specimens into many small beams accelerated the deterioration of the resin-dentin bond in water. In addition, Okuda et al., 2001, reported that when 0.7 mm thick slabs were stored in water and subjected to the microtensile bond strength test, resin-dentin bond strengths decreased over time. The microtensile bond strength (μTBS) test offers several advantages over conventional shear and tensile bond strength tests for evaluating the durability of the dual-cure resin cement-ceramic bond (Foxton *et al.*, 2002; Sano *et al.*, 1994; Shono *et al.*, 1999; Shono *et al.*, 1999). When the μTBS test is employed, the direction of the curing light can be precisely controlled and multiple serial slabs, less than 1 mm thick, can be harvested from one specimen, stored in water, and evaluated at different intervals over a period of time. To date, there is no information on the stability of the bond between silicon oxide ceramic treated with a multi-component liquid ceramic surface treatment and dual-cure resin cement after long-term immersion in water. This in-vitro study evaluated the microtensile bond strength (µTBS) of the dual-cure resin cement/silicon oxide ceramic bond after long-term immersion in water when the ceramic surface was treated with either a ceramic primer, a combination of primer and bonding resin or a ceramic bonding agent. The effect of ceramic thickness on µTBS was also tested. The null hypothesis tested was that the type of multi-component ceramic surface treatment would not affect the long-term durability of the dual-cure resin/silicon oxide ceramic bond.

Materials and Methods

Specimen Preparation

Vita Celay blanks (Vita Zahnfabrik, Bad Säckingen, Germany), shade A2M, were cut using a horizontal diamond cutting saw(Leitz 1600 saw microtome, Ernst Leitz, Wetzlar, Germany) under running water, into multiple slices measuring 12 mm x 10 mm x 1 mm, 2 mm, and 3 mm thick. The surfaces of each ceramic slice were carefully polished using wet 600-grit silicon carbide paper, then cleaned in an ultrasonic water bath for five min. The thickness of each slice was then measured again using digital calipers (Mitutoyo CD15, Mitutoyo Co., Japan) to ensure their final thicknesses were accurate to within 0.1 mm. The materials used in this study are presented in Table 1.

Bonding Procedure

The ceramic slices were then randomly divided into two experimental groups as depicted in Figure 1;

Figure 1. Schematic illustration of specimen preparation for microtensile test

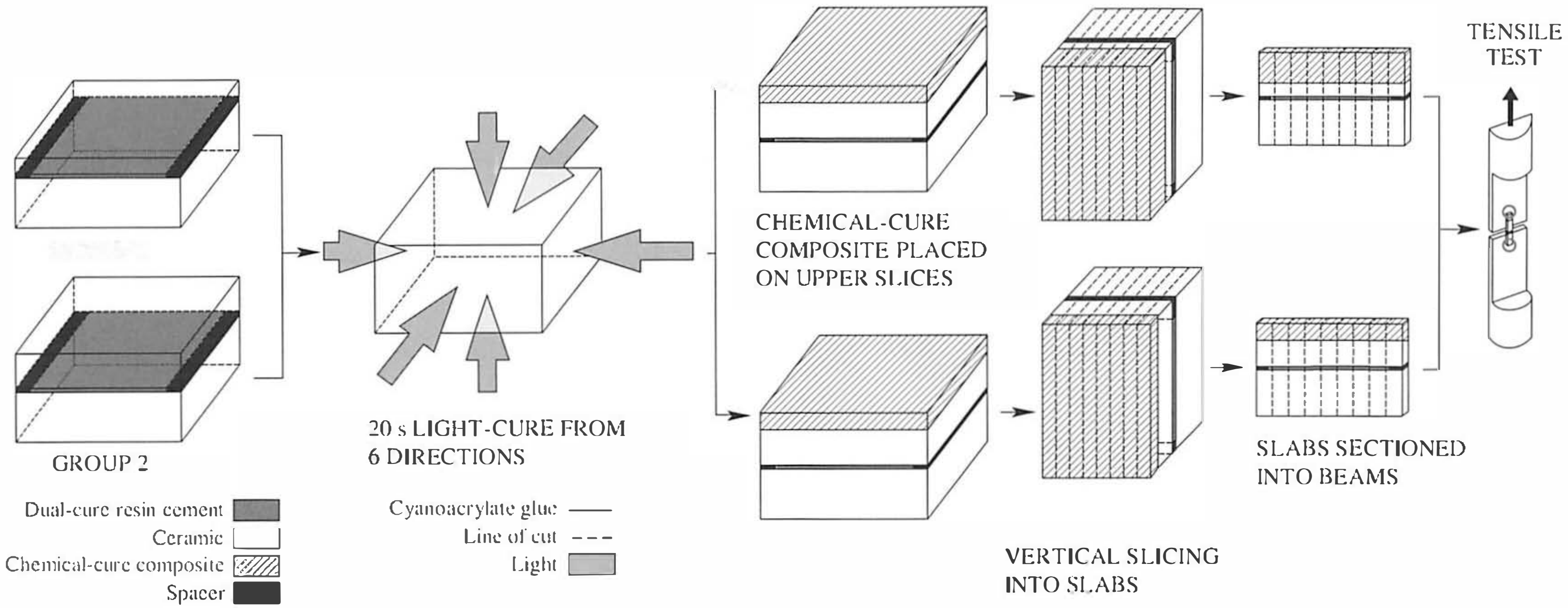


Table 1. Materials tested in this study

Material	Manufacturer	Batch number	Composition
Vita Celay Blank	Vita Zahnfabrik H Rauter Gmbh & Co.KG, Bad Säckingen, Germany	05BY0139	Feldspathic porcelain
K-etchant	Kuraray Co., Osaka, Japan	-	40% H_3P0_4
Clearfil Liner Bond 2V Primer (A + B) (2V Pr)	Kuraray Co., Osaka, Japan	00028A/ 00029A	MDP, HEMA, H_20, chemical and photoinitiators
Clearfil Liner Bond 2V Bond (A + B) (Bd)	Kuraray Co., Osaka, Japan	0065AA/ 0007AB	MDP, dimethacrylates, photoinitiator,accelerators, microfillers
Clearfil Photo Bond (Catalyst + Universal) (P Bd)	Kuraray Co., Osaka, Japan	0305AA/ 0407AA	MDP, HEMA, dimethacrylates, photoinitiator, accelerators, ethanol
Porcelain Bond Activator (PBA)	Kuraray Co., Osaka, Japan	0087A	γ-MPS, monomers
Panavia F (A + B)	Kuraray Co., Osaka, Japan	011182	Filler (78%), MDP, dimethacrylates, chemical and photoinitiators

Table 2. Ceramic Surface Treatments

Sub-group	Phosphoric Acid Treatment	Silane Treatment	Bonding Resin
2VPr	Yes	Clearfil Liner Bond 2V Primer (A+B) and Porcelain Bond Activator	None
2VPr +Bd	Yes	Clearfil Liner Bond 2V Primer (A+B) and Porcelain Bond Activator	Clearfil Liner Bond 2V Bond (A+B)
P Bd	Yes	Clearfil Photo Bond (Cat. + Uni.) and Porcelain Bond Activator	None

Group 1 consisted of three pairs of 1 mm and 3 mm slices, and Group 2, three pairs of 2 mm and 3 mm slices. Two, 200 mm-thick spacers were placed across both ends of the 3 mm-thick ceramic slices in each group. All those 3 mm slices with the spacers attached, were designated as the lower slices. Although the manufacturer of the ceramic blocks recommends hydrofluoric acid etching of the ceramic surface prior to bonding, the manufacturer of the ceramic priming and bonding agents used in the present study recommends treatment of the ceramic surface with phosphoric acid. Treatment of the ceramic surface with phosphoric acid does not etch the ceramic but is said to alter its surface chemistry (Bertolotti *et al.,* 1989). Therefore, the ceramic surfaces to be bonded were treated with 40 % phosphoric acid gel for 10 s, rinsed with water and dried using a 3 in 1 air syringe.

Each group was then further divided into three sub-groups and the ceramic surfaces silanated with one of the following treatments (Table 2); (1) Clearfil Liner Bond 2V Primer / Porcelain Bond Activator (2V Pr), (2) Clearfil Liner Bond 2V Primer / Porcelain Bond Activator followed by the application of Clearfil Liner Bond 2V Bond (2V Pr + Bd), and (3) Clearfil Photo Bond / Porcelain Bond Activator (P Bd) (Kuraray Co., Osaka, Japan) (table 1) in accordance with the manufacturer's instructions. All sub-groups were bonded with a dual-cure resin cement, (Panavia F, Kuraray Co., Osaka, Japan). The ceramic slices were carefully positioned together and a load of 35 g was placed on the upper slice while the excess cement was wiped away with a brush, to ensure even film thickness, and exposed to a conventional light source (Tokuso Powerlite, Tokuyama Co., Tokyo) for 20 s from each of six directions. The tip diameter of the light-guide was 12.25 mm. Prior to each bonding procedure, the power density of the light source was checked with a digital radiometer(Jetlite light tester, J.Morita USA inc., Mason Irvine, CA, USA) to ensure a similar output The mean power density of the light source was 705 ± 4 mW/cm^2. The upper slices were then built up with chemical-cure resin composite (Clearfil FII, Kuraray. Co., Japan) to make grips for attachment to the testing apparatus as depicted in Figure 1. All the bonded specimens were then stored in water at 37 °C for 24 hours.

Bond Strength Testing

After 24 h water storage, each bonded specimen was attached to the arm of a low-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) and nine vertical cuts were made perpendicular to the bonded interface under water-cooling, to harvest eight slabs approximately 0.7 mm thick. Immediately, after one week, six weeks and one year of immersion in water, which was changed every day until testing, two slabs were randomly selected from each sub-group and bonded separately using cyanoacrylate glue(Zapit, DVA, Anaheim, CA, USA) to glass microscope slides (Microslide glass, Matsunami Glass Ind. Ltd., Japan). Another glass slide, bonded to a custom-molded acrylic base-plate which was slotted into the outer casing of the diamond saw, acted as a guide for the transverse slicing of the slabs into beams 6 mm in length and with a mean cross-sectional area of 0.52 ± 0.06 mm², measured using digital calipers. Each slab yielded a maximum of nine beams. Since the first and last beams were not included as these were at the positions of the spacers, the maximum yield from the two slabs was 14 beams.

Using cyanoacrylate glue, each beam was carefully bonded onto a testing device (Bencor-Multi-T, Danville Engineering Co., San Ramon, USA) mounted in a tabletop material testing machine (EZ Test, Shimadzu, Kyoto, Japan), and subjected to a tensile force at a crosshead speed of 1 mm/min.

Laser scanning confocal microscopy

The laser scanning confocal microscope is very convenient for determining the failure mode of debonded ceramic beams because an accurate 3-D image of the de-bonded surface, with no out-of focus blur can be quickly obtained by making and assembling a series optical tomograms (Van Meerbeek *et al.,* 2000). Following bond strength testing, all the failed beams (336) were bonded to brass tablets. Laser scanning confocal microscopy (LSCM)(1LM15W, Lasertec Co., Yokohama, Japan), was initially performed without any subsequent specimen preparation. However, to improve the clarity and contrast of the images, the de-bonded surfaces of the failed beams were gold-sputter coated (Elionix Quick Auto Coater, Elionix, Japan). A transparent grid divided into squares measuring 6 mm x 6 mm (25 % of the bar length) was used to map the percentage of ceramic/resin-cement visible on enlarged micrographs of all the de-bonded surfaces. Failure mode was classified as: A, 100% adhesive failure at the bonded interface; B, More than 50% adhesive failure of the resin cement at the bonded interface; C, Less than 50% adhesive failure of the resin cement at the bonded interface; D, Cohesive failure within the resin cement; and E, Cohesive failure within ceramic.

Statistics

The load at failure divided by the cross-sectional area of the beam was used to calculate the microtensile bond strength (μTBS) in units of stress (MPa). The data were analyzed by a three-way ANOVA factorial analysis (ceramic treatment, ceramic thickness and storage time) and Fisher's PLSD post-hoc test. Statistical significance was considered as $p<0.05$.

Results

The results of the three-way ANOVA are shown in Table 3 and the

Table 3. Results of the three-way analysis of variance:
Dependent variable - bond strength.

			Sum of	Mean	Signif.
Effect	DF	Squares	Square	F-Value	Level
Ceramic treatment	2	10619.19	5309.59	68.98	<0.0001
Storage time	3	26893.94	8964.65	116.47	<0.0001
Ceramic treatment * Storage time	6	6338.44	1056.41	13.72	<0.0001
Thickness	1	2011.99	2011.99	26.14	<0.0001
Ceramic treatment * Thickness	2	622.57	311.28	4.04	0.185
Storage time * Thickness	3	1299.25	433.08	5.63	0.0009
Ceramic treatment * Storage time * Thickness	6	3060.01	510.00	6.63	< 0.0001
Residuals	312	24014.70	76.97		

μTBS test in Table 4. The factors, ceramic treatment, storage time, and thickness had significant main effects ($p<0.0001$). There was a significant interaction between ceramic treatment and storage time ($p<0.0001$), and an interaction between thickness and storage time ($p=0.0009$). There was a significant three-factor interaction between ceramic treatment, storage time, and thickness ($p<0.0001$).

Regarding Group 1, there were no significant differences in μTBS between 2V Pr, 2VPr + Bd, and P Bd after 1 day ($p>0.05$). However, after 1 year of water storage, there were significant differences between all three sub-groups ($p<0.05$). Both 2V Pr and 2V Pr + Bd significantly decreased in μTBS over time, such that after 1 year, μTBS were significantly lower than after 1 day of water storage ($p<0.05$). After 1 year, the μTBS of 2VPr + Bd was significantly higher than that of 2V Pr ($p<0.05$). On the otherhand, P Bd did not significantly reduce in μTBS over time ($p>0.05$). The μTBS of P Bd after 1 year of water storage was similar to that after 1 day, 28.1 ± 14.7 and 30.4 ± 9.7 MPa, respectively.

In the case of Group 2, after 1 day, the μTBS of all three sub-groups were similar, with 2V Pr having the highest μTBS and P Bd the lowest μTBS, 32.0 ± 8.1 and 25.8 ± 9.3 MPa, respectively. After 6 weeks of water storage, the μTBS of 2V Pr + Bd and P Bd were similar to those after 1 day, but the μTBS of 2V Pr had significantly reduced ($p<0.05$). Between six weeks and one year, both 2V Pr + Bd and P Bd significantly decreased in μTBS ($p<0.05$). After one year of water storage, P Bd had the highest μTBS of the three ceramic treatments.

The failure modes of the beams are shown in figure 2. Regarding Group 1, after one day of water storage, all three sub-groups exhibited roughly similar percentages of greater than and less than 50% adhesive failure at the resin-ceramic interface and cohesive failure in resin. However, for all three sub-groups, there was a decrease in the percentage of cohesive failures in resin and an increase in the number of complete adhesive failures over time. Figures 3a

Table 4. Tensile Bond Strength (MPa) of Groups 1 and 2

	TREATMENT	1 DAY		1 WEEK		6 WEEKS		1 YEAR
Gp. 1 (1mm)	2V Pr	31.2 ± 8.3	*NS*	28.0 ± 6.2	$P<0.05$	20.9 ± 7.6	$P<0.05$	0.9 ± 3.2
	2V Pr + Bd	27.5 ± 6.2	$P<0.05$	38.9 ± 6.7	$P<0.05$	18.7 ± 5.4	$P<0.05$	7.7 ± 15.1
	P Bd	30.4 ± 9.7	$P<0.05$	51.7 ± 12.0	$P<0.05$	26.9 ± 4.6	*NS*	28.1 ± 14.7
Gp. 2 (2mm)	2V Pr	32.0 ± 8.1	$P<0.05$	21.2 ± 8.8	$P<0.05$	1.4 ± 4.1	*NS*	0
	2V Pr + Bd	28.2 ± 7.1	*NS*	26.0 ± 9.2	*NS*	26.1 ± 7.1	$P<0.05$	8.4 ± 8.8
	P Bd	25.8 ± 9.3	$P<0.05$	37.0 ± 8.6	$P<0.05$	28.3 ± 7.2	$P<0.05$	17.3 ± 15.0

All values are mean ± SD

The number of tested beams at each time interval = 14

NS = not statistically different ($P>0.05$)

Groups linked by vertical bars are not significantly different ($P>0.05$)

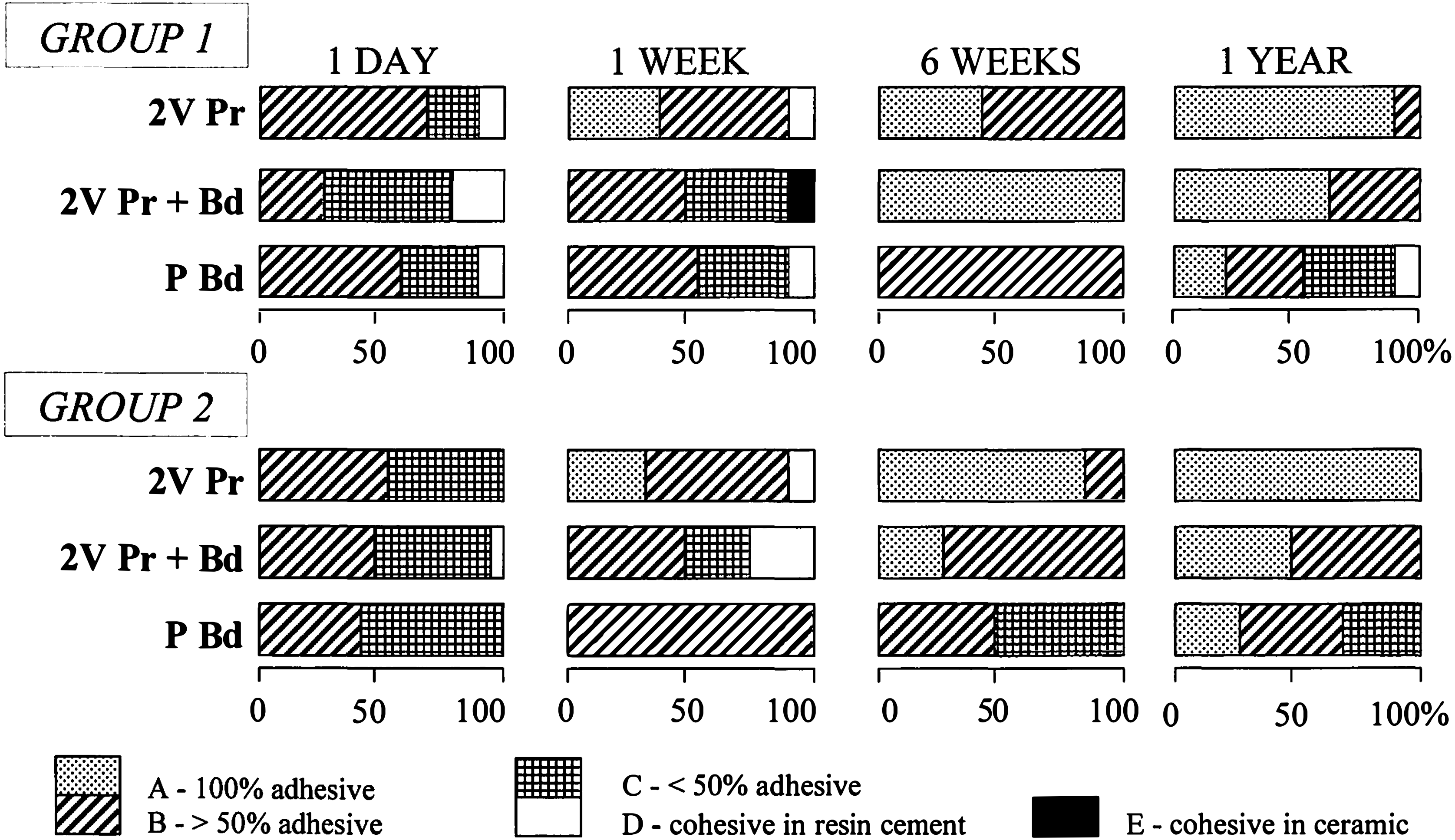
and 3b are representative micrographs of the upper and lower fractured ends of a beam from the 2V Pr sub-group of Group 1 after 1 year, and show complete adhesive failure at the resin-ceramic interface. Figures 4a and 4b are representative micrographs of the upper and lower fractured ends of a beam from the 2V Pr + Bd sub-group of Group 1 after 1 year, and show more than 50% adhesive failure at the resin-ceramic interface. Figures 5a and 5b are representative micrographs of the upper and lower fractured ends of a beam from the P Bd sub-group of Group 1 after 1 year, which exhibit complete cohesive failure within resin. Group 2 exhibited a similar pattern of failure modes to group 1, after 1 day, 1 week, 6 weeks and 1 year of water immersion. In both groups, 2VPr exhibited the highest percentage of complete adhesive failures and P Bd the least, after 1 year of water storage.

Out of a maximum total of 336 beams, 63 failed during preparation for bond strength testing, and these are included in the results as zero bond strengths. 12 were from 2V Pr after six weeks and 27 after one year, which were all complete adhesive failures. 17 were from 2V Pr + Bd after one year, which were all adhesive failures and 7 were from P Bd after one year, which were greater than 50% adhesive failures.

Discussion

There is limited information on the durability of the bond between dual-cure resin cement and ceramic treated with a multi-component ceramic surface treatment, when immersed for a long period in water. The results of the present experiment found that after 1 year of water immersion, there were significant differences in μTBS between the three kinds of multi-component ceramic surface treatments. Therefore, the null hypothesis that the type of multi-component ceramic surface treatment does not affect the durability of the dual-cure resin cement/silicon oxide ceramic bond has to be rejected.

Figure 2. Classification of specimen failure mode



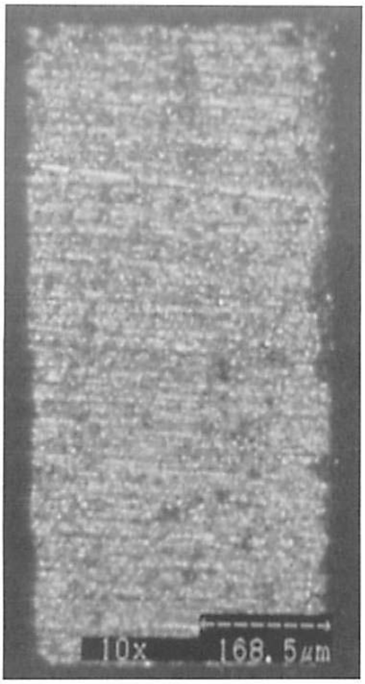


Fig. 3a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the 2V Pr sub-group in Group 1 showing complete adhesive failure after one year of water storage. (magnification X250)

Fig. 3b Lower de-bonded surface of the same beam as 3a. (magnification X250)

Fig. 4a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the 2V Pr + Bd sub-group in Group 1, exhibiting >50% adhesive failure at the bonded interface after one year of water storage. (magnification X250)

Fig. 4b Lower de-bonded surface of the same beam as 4a. (magnification X250)

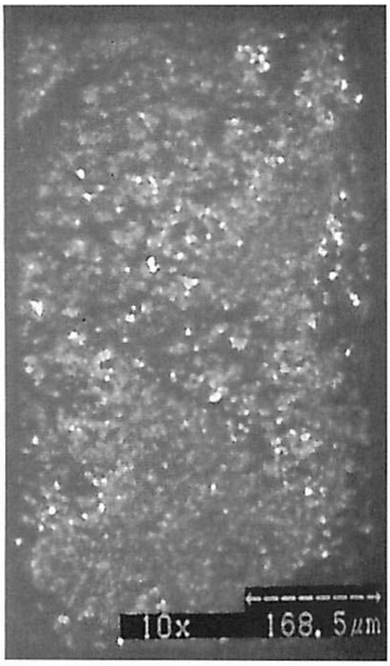


Fig. 5a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the P Bd sub-group in Group 1, exhibiting cohesive failure in resin after one year of water storage. (magnification X250)

Fig. 5b Lower de-bonded surface of the same beam as 5a. (magnification X250)

In both groups, the μTBS of the sub-groups treated with 2V Pr significantly decreased after immersion in water for one year and was accompanied by an increase in the percentage of complete adhesive failures at the resin-ceramic interface. For Group 1, a significant reduction was seen after 6 weeks of water immersion, whereas for Group 2, this occurred after only 1 week of water storage. A significant reduction in bond strength indicates hydrolytic degradation of the resin-ceramic bond (Roulet, 1987). In our previous study, using 3 mm-thick ceramic silanated with 2V Pr/PBA, bond strength significantly reduced after one week of immersion in water (Foxton *et al.,* 2001). The reason for the susceptibility of the dual-cure resin cement-ceramic bond to hydrolytic degradation after priming with 2V Pr/PBA, most likely lies in the chemical composition of this particular multi-component ceramic primer (table 1). 2V Pr/PBA is a ceramic priming system made up of a two-bottle self-etching dentin primer and a separate silane coupling agent. 2V Pr is a self-etching dentin primer, whose chemical components include chemical initiators, photoinitiators, water, the hydrophilic monomer, HEMA and the phosphate monomer, MDP (Okada *et al.,* 1998). When PBA, which contains the silane coupling agent, γ-methacyloxypropyl trimethoxysilane (γ-MPS), is mixed with 2V Pr, the alkoxy groups of γ-MPS are hydrolyzed into silanol groups and then activated by acid catalytic action with the phoshate monomer, MDP, contained in the primer (Okada *et al.,* 1998). Prior to the application of the 2VPr/PBA mixture to the ceramic surface, the ceramic surface was treated with phosphoric acid since this is the recommendation of the manufacturer of the ceramic surface treatments although the manufacturer of the tested ceramic recommends etching of the ceramic surface with hydrofluoric acid. Treatment of the ceramic surface with phosphoric acid is thought to alter ceramic surface chemistry by the addition of a hydrogen atom to the silica network(Bertolotti *et al.,* 1998). When the 2VPr/PBA mixture is applied to the ceramicsurface, the activated γ-MPS reacts with the silanol groups on the ceramic surface(Okada *et al.,* 1998). Therefore, after application of 2V Pr /PBA to the ceramic surface, water still remains because it is incorporated in the solvent, does not evaporate and is not involved in the formation of the silanol groups. We speculate that in the present experiment, the susceptibility of the dual-cure resin-cement/ceramic bond to hydrolytic degradation was due to the presence of hydrophilic chemical components, in particular water, in 2V Pr. After complete degradation of the siloxane bonds had occurred, the resin-ceramic bond had only micro-mechanical retention to rely upon. The fact that the onset of a significant in reduction in μTBS occurred between 1 and 6 weeks water storage in Group 2 compared to between 6 weeks and 1 year in Group 1 indicates that ceramic thickness had a significant effect on bond durability, even though the light source was aimed from multiple directions directly at the resin layer. This would imply that when the ceramic surface was silanated using 2V Pr/PBA, the bonding ability of Panavia F is dependent upon adequate exposure light and can be affected by the thickness of the ceramic restoration.

In the present study, the additional application of an adhesive bonding resin to the ceramic surface silanated using 2V Pr/PBA, improved the durability of the resin-ceramic bond. After 1 year of water immersion, the μTBS of 2V Pr + Bd in Group 1 and Group 2 were similar. In addition, both groups exhibited similar failure modes, a mixture of complete adhesive and greater than 50% adhesive failure at the resin-ceramic interface. This result indicates that applying an adhesive bonding resin to a ceramic surface silanated with 2V Pr/PBA, improves the resistance of the resin-ceramic bond to hydrolytic degradation. When 2V Pr/PBA is applied to the ceramic, the solvent does not evaporate but remains on the surface and can therefore easily mix with 2V Bd. We speculate that when the dual-cure resin cement was polymerized, a more hydrophobic resin-ceramic interface was created which offered more resistance to hydrolytic degradation. In addition, for this particular ceramic surface treatment, dual-cure resin-ceramic bond durability was not affected by ceramic thickness when ceramic thickness was less than or equal to 2 mm and exposure to light was from multiple directions.

Previous research demonstrated that when air-abraded feldspathic ceramic specimens, treated with P Bd/PBA and bonded with dual-cure resin cement, were subjected to 20 000 thermal cycles, no significant reduction in shear bond strength occurred (Matsumura *et al.,* 1997). In the present study, treatment of the ceramic surface with phosphoric acid and then with P Bd/PBA, created the most durable dual-cure resin-ceramic bond of the three surface treatments. In the case of Group 1, μTBS after 1 year of water immersion was similar to that after one day. Failure mode analysis revealed that all the beams had failed cohesively in resin, indicating a strong resin-ceramic bond. Although, the P Bd specimens in Group 2 showed a significant reduction in μTBS after 1 year, which was accompanied by an increase in the percentage of 100% adhesive failures, μTBS were the highest among the three ceramic surface treatments. P Bd/ PBA is a ceramic bonding agent consisting of a two-bottle dentin bonding agent (P Bd) and a separate silane coupling agent (PBA). As mentioned previously, the silane coupling agent is activated by a phosphate monomer, also MDP. However, although the chemical components of P Bd are similar to 2VPr, P Bd does not contain water. Instead, ethanol and dimethacrylate components are present (table 1). These particular chemical components make P Bd more hydrophobic that 2VPr and may also increase its wetting ability. When P Bd is applied to a ceramic surface, the ethanol will evaporate on gentle air-drying. We therefore speculate that the bond strengths of the P Bd primed sub-groups were higher after 1 year because the dual-cure resin/ceramic bond was more resistant to hydrolytic degradation as a result of the resin-ceramic interface being hydrophobic.

Ceramic thickness has a significant effect on the mechanical properties of dual-cure resin cement and it's bonding to ceramic (Blackman *et al.*, 1990; El-Mowafy *et al.,* 1999; Foxton *et al.,* in press). However, there is limited information on the effect of ceramic thickness on bond strength after long-term immersion in water. The present study used ceramic specimens, 1 and 2 mm thick, which approximately represents a range of thickness for a porcelain veneer and found that after 1 day, bond strengths were similar between the two groups. However, after 1 year of water immersion, whereas five of the subgroups showed significant reductions in tensile bond strength, P Bd/PBA in Group1, did not. This result indicates that this particular ceramic bonding system exhibits good bond durability. However, there appears to be a complex interaction between ceramic thickness, ceramic primer/bonding agent, and water storage time and therefore, further research is needed.

In conclusion, the present study found that the type of multi-component ceramic surface treatment had a significant effect on the long-term durability of the dual-cure resin/silicon oxide ceramic bond. Also, ceramic thickness was found to have a significant effect. However, the effect of ceramic thickness depended upon the type of multi-component ceramic surface treatment used. The presence of water in 2V Pr, resulted in the ceramic primer 2V Pr/PBA forming a significantly less durable resin-ceramic bond than the ceramic bonding agent, P Bd/PBA. The additional application of a bonding resin, improved the durability of 2V Pr/PBA. Therefore, in the case of multi-component ceramic surface treatments that are based on a self-etching dentin primer or dentin bonding agent in conjunction with a separate silane coupling agent, the more hydrophobic the multi-component ceramic surface treatment is, the greater the long-term durability of the dual-cure resin/silicon oxide ceramic bond.

Chapter 4

Relationship between ceramic primer and ceramic surface pH on the bonding of dual-cure resin cement to ceramic

Introduction

It is generally recommended when bonding machined silicon oxide ceramic restorations, to etch the ceramic surface with hydrofluoric acid before applying a silane coupling agent and a resin cement, in order to obtain a clean micro-mechanically retentive surface (Roulet and Degrange, 1996; Thordrup *et al.*, 1999). Hydrofluoric acid etching followed by the application of a silane coupling agent enhances the resin/ceramic bond (Jardel *et al.*, 1999), however hydrofluoric acid is a hazardous substance particularly if used for intra-oral ceramic repairs (Peutzfeld, 2001). Recent developments in polymer chemistry have lead to the development of a new generation of ceramic primers (Aida *et al.*, 1995; Sato *et al.*, 1999). They generally consist of two or three solvents, one of which contains a silane coupling agent, usually γ-methacyloxylpropyl-trimethoxysilane (γ-MPS), and the other, an acidic monomer to catalyse the coupling reaction (Aida *et al.*, 1995; Sato *et al.*, 1999).

Previous research has demonstrated that this new generation of ceramic primers can strongly couple resin cement to machinable ceramic without prior sandblasting or hydrofluoric acid etching of the ceramic surface (Sato *et al.*, 1999; Kamada *et al.*, 1998; Kamada *et al.*, 2001; Foxton *et al.*, in press; Foxton *et al.*, 2002). When using some of these new generation ceramic primers, treatment of the ceramic surface with phosphoric acid is sometimes recommended. The rationale for this is unclear, since scanning electron microscopy has shown that phosphoric acid does not etch ceramic (Aida *et al.*, 1995). Phosphoric acid has been reported to alter ceramic surface chemistry (Bertolotti *et al.*, 1989), how ever there is to date, no published information on how phosphoric acid alters ceramic surface chemistry, or whether there is any interaction between phosphoric acid and the ceramic primer when bonding resin cement to ceramic.

Research on the effects of acid on ceramic surface chemistry has been limited to electron dispersive spectroscopy (EDS) analysis of the ceramic surface (Canay *et al.,* 2001). Canay et al observed the effect of applying HF acid for different periods of time on the ceramic surface and found that there were changes in the concentration of F, Si, Al, K,Ca and Na in the etched zone, and they contributed these changes to the formation of reaction products of fluorosilicate (Canay *et al.,* 2001). However, their effect on bond strength was not tested. The disadvantage of EDS is that although it can detect the concentration of constituent elements present on the surface of the substrate, it cannot detect changes in hydrogen ion concentration, which might occur in the presence of an acidic substance. Recently, a new type of imaging microscope called a scanning chemical microscope based on a flat pH-imaging semiconductor silicon sensor has been developed(Nomura *et al.,* 1997; Nomura *et al.,* 2000; Kitasako *et al.,* 2002; Nomura *et al.,* 2001). This sensor can function as an array of multiple pH sensing spots and is able to detect the presence of hydrogen ions on a solid material placed on an electrolyte (Nomura *et al.,* 1997; Nomura *et al.,* 2000; Kitasako *et al.,* 2002; Nomura *et al.,* 2001). A photoelectrical current, which is dependent upon the amount of protons, can be obtained when the underside of the sensor is illuminated by a light source with a bias voltage applied between the underside and the electrolyte solution placed on the upper surface (Nomura *et al.,* 1997; Nomura *et al.,* 2000; Kitasako *et al.,* 2002; Nomura *et al.,* 2001). When the illuminated area is scanned, multiple point pH measurements can be obtained (Nomura *et al.,* 1997; Nomura *et al.,* 2000; Kitasako *et al., 2002*; Nomura *et al.,* 2001). The resulting pH dependent electrical signal at each measurement point is fed to a computer and analyzed using image analysis software (Nomura *et al.,* 1997; Nomura *et al.,* 2000; Kitasako *et al.,* 2002; Nomura *et al.,* 2001).

There is currently no information on the effect of acid on ceramic surface pH.

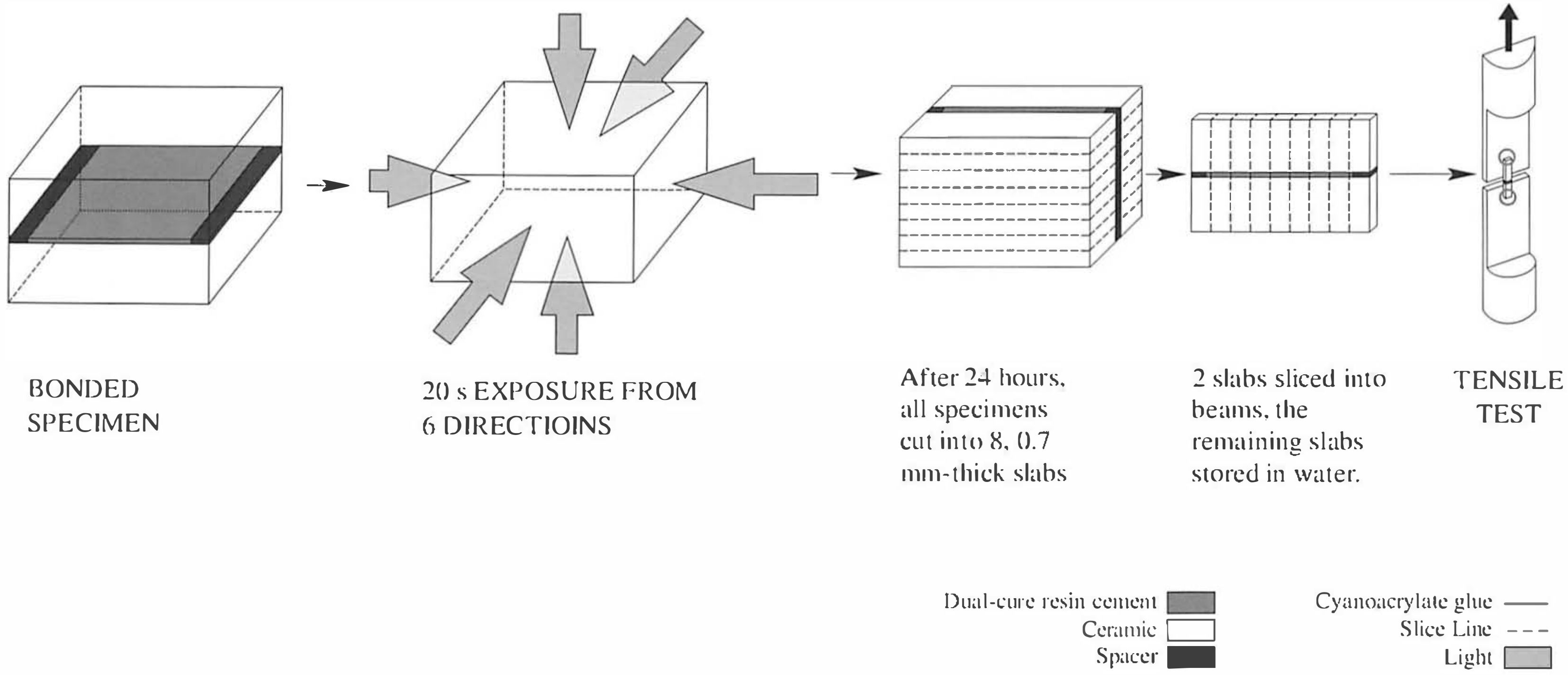
The purpose of the present study was to examine the relationship between the ceramic primer and ceramic surface pH on the microtensile bond strength of dual-cure resin cement to silicon oxide ceramic. Ceramic surface pH was measured using a scanning chemical microscope and ceramic surface morphology was evaluated using scanning electron microscopy. Two ceramic primers were tested, one commercially available and the other, an experimental ceramic primer formulated without the inclusion of phosphate monomer. Two acidic treatments were used, hydrofluoric acid and phosphoric acid and after application of the acid, the ceramic surface was rinsed with water for different periods of time. The null hypotheses tested were (1) The ceramic primer and acidic treatment would not affect the microtensile bond strength of dual-cure resin cement to ceramic, and (2) The application of phosphoric or hydrofluoric acid and the water rinsing time would not affect the pH of the ceramic surface.

Materials and Methods

Sample Preparation

Vita Celay blanks (Vita Zahnfabrik, Bad Säckingen, Germany), shade A2M, were cut using a horizontal diamond cutting saw(Leitz 1600 saw microtome, Ernst Leitz, Wetzlar, Germany) under running water, into multiple slices measuring 12 mm x 10 mm x 3 mm thick. The surfaces of each ceramic slice were carefully polished using wet 600-grit silicon carbide paper, then cleaned in an ultrasonic water bath for five minutes. The thickness of each slice was then measured again using digital calipers (Mitutoyo CD15, Mitutoyo Co., Kawasaki, Japan) to ensure their final thicknesses were accurate to within 0.1 mm. The materials used in this study are presented in Table 1.

Figure 1. Schematic illustration of specimen preparation for microtensile tests



Microtensile Bond Strength Test

14 pairs of ceramic slices were then randomly selected and divided into two groups of 6 pairs and one group of two pairs, and subjected to the following acidic treatments: (a) The ceramic surfaces of one group of 6 pairs were treated with 40 % phosphoric acid gel (K-etchant, Kuraray Medical Co., Osaka, Japan) (PA) for 10s. 2 pairs were then rinsed with water using a 3-in-1 air-syringe for 15 s (PA-15); 2 pairs were rinsed with water for 30 s (PA-30); and 2 pairs rinsed for 60 s (PA-60), (b) the ceramic surfaces of the other group of six pairs were treated with 20 % hydrofluoric acid (HFA) for 10 s, 2 pairs were then rinsed with water for 15 s (HFA-15); 2 pairs were rinsed with water for 30 s (HFA-30); and 2 pairs rinsed for 60 s (HFA-60), (c) the ceramic surfaces of the group of 2 pairs were left untreated (the controls (C)). Two, 200 µm-thick spacers were placed across both ends of one slice of each pair. All those slices with the spacers attached, were designated as the lower slices.

The 14 pairs were then divided equally into two experimental groups. The surfaces to be bonded of one group were treated with a commercially available ceramic primer (Tokuso Ceramics Primer, Tokuyama Dental Corp., Tokyo, Japan) (TCP), and the other group with an experimental ceramic primer formulated without phosphate monomer (Experimental, Tokuyama Dental Corp., Tokyo, Japan) (TCP-NoPM). All the pairs were bonded with dual-cure resin cement, (Bistite II, Tokuyama Dental Corp., Tokyo, Japan). The ceramic slices were carefully positioned together and a load of 35 g was placed on the upper slice while the excess cement was wiped away with a brush, to ensure an even film thickness, and exposed to a conventional light source (Tokuso Powerlite, Tokuyama Dental Corp., Tokyo) for 20 s from each of six directions. The tip diameter of the light-guide was 12.25 mm. Prior to each bonding procedure, the power density of the light source was checked with a digital radiometer (Jetlite light tester, J.Morita USA inc., Mason Irvine, CA, USA) to ensure that the power density of the light source was between 700 and 710 mW/ cm^2. All the bonded specimens were then stored in water at 37 °C for 24 hours.

After 24 h water storage, each bonded specimen was attached to the arm of a low-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) and nine vertical cuts were made perpendicular to the bonded interface under water-cooling, to harvest eight slabs approximately 0.7 mm thick, as described by Foxton *et al*, in press, previously. Two slabs were randomly selected from each sub-group and bonded separately using cyanoacrylate glue (Zapit, DVA, Anaheim, CA, USA) to glass microscope slides (Microslide glass, Matsunami Glass Ind. Ltd., Tokyo, Japan). The other six slabs were kept in storage for a later durability study. Another glass slide, bonded to a custom-molded acrylic base-plate which was slotted into the outer casing of the diamond saw, acted as a guide for the transverse slicing of the slabs into beams 6 mm in length and with a mean cross-sectional area of 0.48 ± 0.07 mm^2, measured using digital calipers as shown in Fig. 1. Each slab yielded a maximum of nine beams. Since the first and last beams were not included as these were at the positions of the spacers, the maximum yield from the two slabs was 14 beams.

Using cyanoacrylate glue, each beam was carefully bonded onto a testing device (Bencor-Multi-T, Danville Engineering Co., San Ramon, USA) mounted in a tabletop material testing machine (EZ Test, Shimadzu, Kyoto, Japan), and subjected to a tensile force at a crosshead speed of 1 mm/min. The load at failure divided by the cross-sectional area of the beam was used to calculate the microtensile bond strength (μTBS) in units of stress (MPa).

Following bond strength testing, all the failed beams (196) were bonded to brass tablets. Laser scanning confocal microscopy (LSCM) (1LM15W, Lasertec Co., Yokohama, Japan), was initially performed without any subsequent specimen preparation. However, to improve the clarity and contrast of the images, the de-bonded surfaces of the failed beams were gold-sputter coated (Elionix Quick Auto Coater, Elionix, Tokyo, Japan) (Foxton *et al.*, in press). Failure mode was classified as: A, 100% adhesive failure at the bonded interface; B, Mixed cohesive/adhesive failure of the resin cement at the bonded interface; C, Cohesive failure within the resin cement; and D, Cohesive failure within ceramic.

Scanning Chemical Microscope (SCHEM)

9 ceramic slices were randomly selected, and cut into quarters (2.5 x 2.0 x 3.0 mm) using a low-speed diamond cutting saw to make 7 experimental groups of five specimens. 1 group was left untreated (control); 3 groups were treated with PA and subjected to the same water rinsing times as described previously for the bond strength test (PA-15, PA-30, and PA-60); and 3 groups were treated with HF acid and rinsed with water as described previously (HFA-15, HFA-30, and HFA-60).

To set up the measurement using the scanning chemical microscope (SCHEM-100, Horiba, Ltd., Kyoto, Japan), an agar solution, consisting of 1.5% agar powder and 0.1M Potassium Chloride was heated. Two 1-mm thick plastic spacers were placed on the surface of a flat semiconductor silicon sensor at either end. An acrylic block was positioned on top of the spacers and then slightly tilted while the warm agar solution was gently pipetted onto the sensor. The pH value of the agar solution was then measured using a pH meter (TWIN pH, Horiba Ltd., Kyoto, Japan). This pH value was used to calibrate the flat pH sensor and to convert the photocurrent signal of the sensor to the pH value (Nomura *et al.*, 2001).

After the agar had solidified, the acrylic block was carefully lifted off, and each ceramic specimen was positioned, one at time, on the agar film, and then the sensor was placed into the microscope. Any protons or hydroxides released into the agar film were detected at the bottom of the agar film by the flat semiconductor silicon sensor. The protons or hydroxides were detected as a change in the photocurrent value generated in the sensor and then, converted to pH values. Although these pH values were not the actual pH of the specimen surface but those of the agar film, these values reflected the surface acidic or basic condition of the specimen. Therefore, the pH values obtained in this study were regarded as the surface pH of the specimen and were used for further evaluations.

To measure the surface pH of the specimen, the photocurrent signals were measured at 75 x 75 measurement points on the sensor at 200 μm-thick intervals. The photocurrent was stored in a PC and displayed as a tagged image file format (TIFF) image using image analysis software (Image-Pro Plus, Media Cybernetics, L.P., MD, U.S.A) (IPP). The time required to obtain a set of photocurrent values was 180 s. The set of photocurrent values was obtained three times with 15 min intervals. The TIFF image was analyzed in gray-scale mode. In gray-scale mode, pixels of low intensity corresponded to points of high pH and pixels of high intensity, to points of low pH. The line profile analysis tool of IPP was used to determine first, the region of lowest pH, then the region of highest pH. This was done by, positioning straight lines over the TIFF images. Measurements were performed three times on each TIFF image and the means calculated. The pH value was obtained by entering the pixel intensities into a custom software program (EXCEL, Microsoft Corp., Redmond, U.S.A). The measurement conditions mentioned here were the optimum, determined by previous pilot studies, to let protons or hydroxides diffuse sufficiently through the agar film.

Scanning Electron Microscopy

3 polished ceramic slices were randomly selected and cut into thirds. 7 specimens were selected, 1 was left untreated (control) and 6 were subjected to each of the acidic treatments (PA-15, PA-30, PA-60, HFA-15, HFA-30, and HFA-60). The specimens were then bonded to brass tablets, gold sputter coated and their surface morphology examined under an SEM (JSM-5310, JEOL, Tokyo, Japan).

Statistics

The bond strength data were analyzed by a three-way ANOVA factorial analysis (etchant, primer and rinsing time) and the pH data using Fisher's PLSD post-hoc test ($P<0.05$). Statistical analysis of the failure modes was performed using the Kruskal-Wallis rank test. For this, each failure mode was given a score from 1 to 4 prior to statistical analysis(Matsumura *et al.,* 1997). A score of 1 was given for 100% adhesive failure at the bonded interface, a score of 2 for mixed adhesive/cohesive failure of the resin cement at the bonded interface, 3 for cohesive failure within resin cement; and 4 for cohesive failure within ceramic. The higher the score, the stronger was the bond (Matsumura *et al.,* 1997).

Results

The microtensile bond strength (μTBS) test data together with the statistical analysis are presented in Table 2 and the pH values of the ceramic surface after the different acidic treatments in Table 3. The failure modes of the beams are shown in Table 4 with the results of the Kruskal-Wallis rank test presented in Table 5.

Three-way ANOVA of the bond strength data without the control groups, revealed that while the primer and rinsing time had significant effects ($p<0.001$), there were no significant interactions between etchant and rinsing time, $p=0.163$, and etchant and primer, $p=0.082$. When no acidic treatment was applied to the ceramic surface, the μTBS of the TCP group was significantly higher than that of the TCP-NoPM group ($p<0.05$). However, when the ceramic surface was treated with either phosphoric or hydrofluoric acid and rinsed for 15 s, there was a significant increase in the μTBS of the TCP-NoPM group ($p<0.05$). On the otherhand, in the case of TCP, treatment of the ceramic surface with either phosphoric or hydrofluoric acid did not significantly increase μTBS

($p>0.05$). Regarding ceramic surface pH, after phosphoric or hydrofluoric acid was applied to the ceramic surface and rinsed for 15 s, significant reductions in surface pH occurred ($p<0.05$), however, there were no significant differences in surface pH between the two acids ($p>0.05$). When rinsing time was increased, surface pH increased, with a significant increase occurring when the rinsing time was increased from 15 s to 60 s for both acidic treatments ($p<0.05$). For each rinsing period, there were no significant differences in surface pH between phosphoric and hydrofluoric acid treatments ($p>0.05$).

Considering the failure modes of the beams, for TCP, the predominant failure mode for all of the sub-groups was a mixture of adhesive and cohesive failure of the resin cement at the bonded interface. Figures 2a and 2b are representative LSM views of the upper and lower de-bonded surfaces of a failed beam from the control group. However, in the case of TCP-NoPM, almost all the specimens of the control (Figs. 3a and b) and PA-60 sub-groups failed adhesively at the bonded interface. On the other hand, all the other TCP-NoPM subgroups treated with either phosphoric or hydrofluoric acid, exhibited a mixture of adhesive and cohesive failure of the resin cement at the bonded interface (Figs 4a and b).

Representative low and high magnification SEM views of the ceramic surfaces of the control, PA-15 and HFA-15 sub-groups are shown in Figs 5a and b, 6a and b and 7a and b, respectively. These show that phosphoric acid did not have a marked effect on the ceramic surface, which had a similar appearance to the control specimen. On the otherhand, hydrofluoric acid created a lattice-like porous surface structure.

Out of a maximum total of 196 beams, 27 failed during preparation for bond strength testing, and these are included in the results as zero bond strengths. 12 were from TCP-NoPM control group, 1 was from TCP-NoPM PA-30, 8 were from TCP-NoPM PA-60 and 6 were from TCP-NoPM HFA-60. These were all 100% adhesive failures.

Table 1. Materials, manufacturer, batch numbers and composition

Material	Manufacturer	Batch number	Composition
Vita Celay Blank	Vita Zahnfabrik H Rauter GmbH & Co.KG Bad Säckingen, Germany.	05BY0139	Feldspathic porcelain
Tokuso Ceramic Primer (A + B) (TCP)	Tokuyama Dental Corp., Tokyo, Japan	310500	Phosphate monomer, γ-methacyloxypropyl trimethoxysilane ethanol
Experimental (TCP-NoPM)	Tokuyama Dental Corp., Tokyo, Japan	310500	γ-methacyloxypropyl trimethoxysilane, ethanol
Bistite II (A + B) (BisII)	Tokuyama Dental Corp., Tokyo, Japan	A13871	Filler (77%), Bis-GMA, MAC-10, chemical initiators, photoinitiators

Table 3.
Change in pH of the ceramic surface after the different acidic treatments

Treatment	Surface pH	Mean change in pH
Control	6.27 (0.23)^{a}	-0.03
PA-15	4.29 (0.27)^{b}	-2.01
PA-30	4.72 (0.41)^{bc}	-1.58
PA-60	5.58 (0.39)^{cd}	-0.72
HFA-15	4.33 (0.25)^{bc}	-1.97
HFA-30	4.84 (0.08)^{cf}	-1.46
HFA-60	5.25 (0.05)^{df}	-1.05

All pH values are mean (SD)
Number of specimens in each group = 5
Values with the same supercript letter are not significantly different ($p>0.05$)
Change in pH is the difference between gel pH and surface pH.
Where mean gel pH = 6.3 (0.1)

Table 2. Microtensile bond strength (MPa) of the two ceramic primers with different acidic treatments

Ceramic Primer		Phosphoric acid (rinsing time (s))			Hydrofluoric acid (rinsing time(s))		
	Control	15	30	60	15	30	60
TCP	31.3 (7.8)^{a}	33.0 (6.6)^{ab}	36.8 (7.8)$^{a-c}$	28.0 (8.9)^{abd}	29.4 (11.4)^{abdei}	29.7 (6.5)$^{a-e,fi}$	30.4 (12.2)$^{a-g,i}$
TCP-No PM	5.5 (12.2)^{h}	30.0 (4.4)$^{a-d,i}$	19.4 (13.4)^{j}	8.2 (11.7)^{hk}	24.7 (13.2)^{abdfgijk}	23.0 (6.9)^{dfijl}	17.1 (5.3)^{jl}

All values are mean (SD)
Number of tested specimens in each group is 14
Groups identified with the same superscript letter are not significantly different ($P>0.05$)

Table 4. Classification of failure mode

	TCP							TCP-NoPM						
		PA			HF				PA			HF		
	C	15	30	60	15	30	60	C	15	30	60	15	30	60
A	0	0	0	0	0	0	0	12	0	1	8	0	0	6
B	11	11	12	13	12	11	11	2	12	13	6	12	12	6
C	3	2	2	1	2	3	3	0	2	0	0	2	2	2
D	0	1	0	0	0	0	0	0	0	0	0	0	0	0

A: Complete adhesive failure at the resin cement-ceramic interface.
B: Mixed cohesive/adhesive failure of the resin-cement at the resin cement-ceramic interface.
C: Complete cohesive failure within resin cement.
D: Complete cohesive failure within ceramic.

Table 5.

Failure modes after microtensile test and Kruskal-Wallis mean rank

	No. of specimens for each failure mode (failure mode/score)				
Sub-group	A/1	B/2	C/3	D/4	Kruskal-Wallis rank
TCP/PA-15	0	11	2	1	118.393
TCP-C	0	11	3	0	117.500
TCP/HFA-30	0	11	3	0	117.500
TCP/HFA-60	0	11	3	0	117.500
TCP/PA-30	0	12	2	0	111.500
TCP-NoPM/PA-15	0	12	2	0	111.500
TCP/HFA-15	0	12	2	0	111.500
TCP-NoPM/HFA-15	0	12	2	0	111.500
TCP-NoPM/HFA-30	0	12	2	0	111.500
TCP/PA-60	0	13	1	0	105.500
TCP-NoPM/PA-30	1	13	0	0	93.393
TCP-NoPM/HFA-60	6	6	2	0	74.857
TCP-NoPM/PA-60	8	6	0	0	50.643
TCP-NoPM-C	12	2	0	0	26.214

Fig. 2a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the TCP control group. Mixed adhesive/cohesive failure at the resin/ceramic interface is evident. (magnification X250)

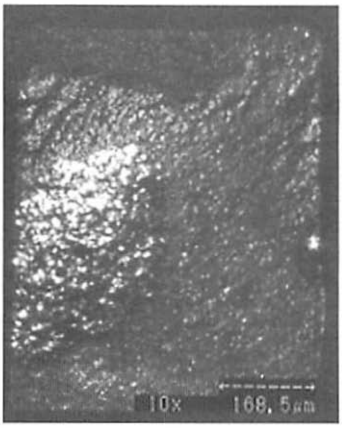


Fig. 2b Lower de-bonded surface of the same beam as 2a. (magnification X250)

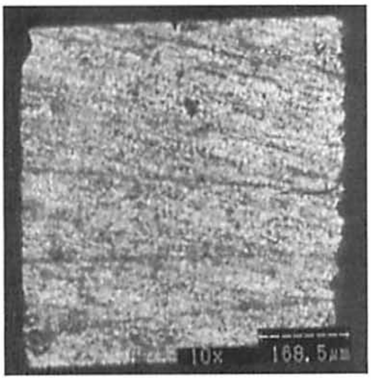


Fig. 3a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the TCP-NoPM control group exhibiting adhesive failure at the bonded interface. (magnification X250)

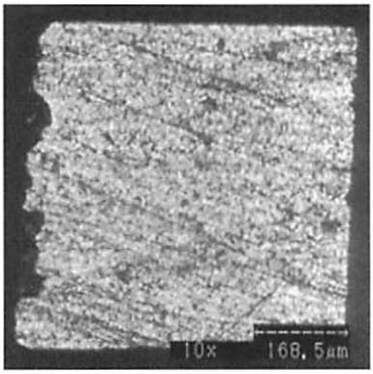


Fig. 3b Lower de-bonded surface of the same beam as 3a. (magnification X250)

Fig. 4a Representative LSCM micrograph of the upper de-bonded surface of a failed beam from the TCP-NoPM PA-15 sub-group. Mixed adhesive/cohesive failure at the resin/ceramic interface is evident. (magnification X250)

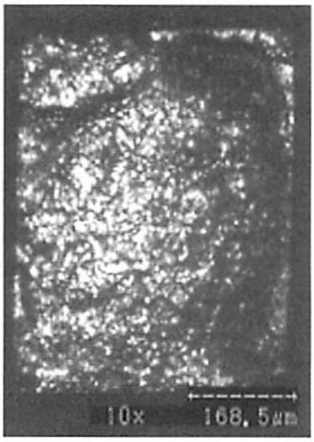


Fig. 4b Lower de-bonded surface of the same beam as 4a. (magnification X250)

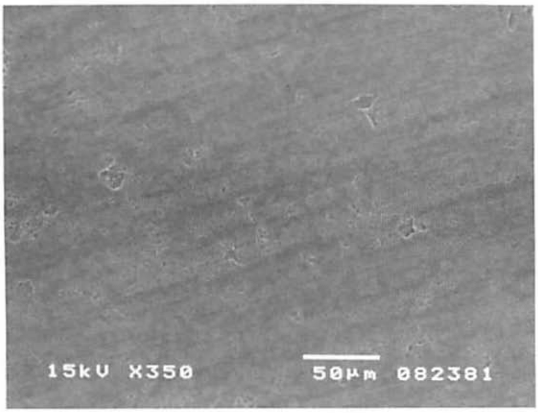


Fig. 5a SEM of the polished ceramic surface in the control group. (magnification X 350)

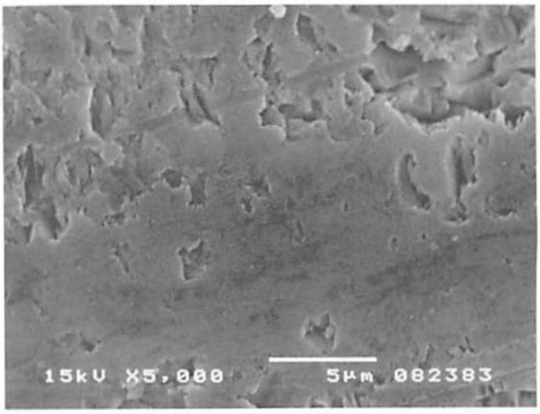


Fig. 5b High magnification (X 5000) SEM of 5a.

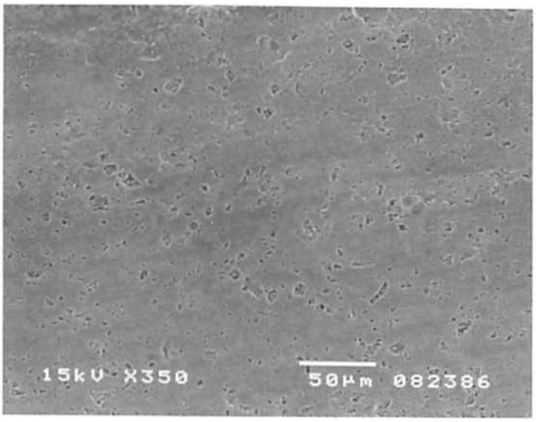


Fig. 6a SEM of the polished ceramic surface after application of 40% phosphoric acid for 10 s followed by 15s water rinsing (PA-15). (magnification X 350)

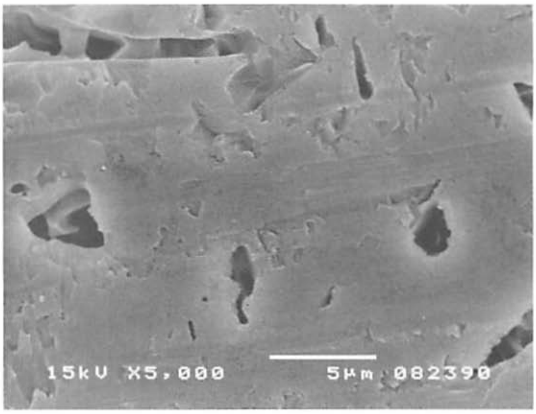


Fig. 6b High magnification (X 5000) SEM of 6a.

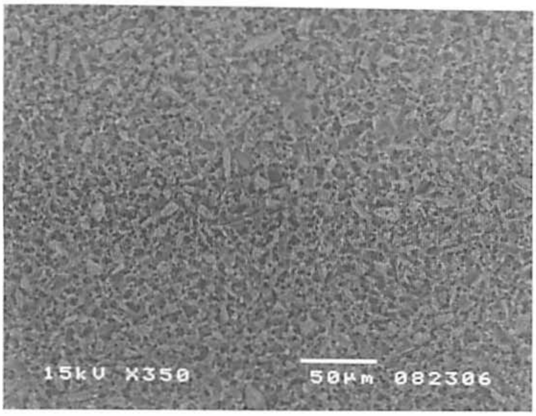


Fig. 7a SEM of the polished ceramic surface after application of 20% hydrofluoric acid for 10 s followed by 15s water rinsing (HFA-15). (magnification X 350)

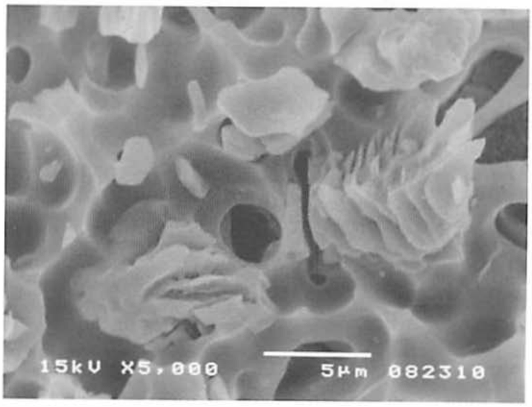


Fig. 7b High magnification (X 5000) SEM of 7a

Discussion

Previous research has shown that a ceramic primer consisting of separate solutions of an acidic monomer and the silane coupling agent, γ-MPS, is able to strongly couple dual-cure resin cement to silicon oxide ceramic (Aida *et al.*, 1995; Sato *et al.*, 1999; Kamada *et al.*, 1998; Kamada *et al.*, 2001; Foxton *et al.*, in press). Although it has been reported that the purpose of the acidic monomer is to activate γ-MPS by acid hydrolysis, enabling it form siloxane bonds with the silicon oxide ceramic surface (Aida *et al.*, 1995), no data has been published on whether γ-MPS can be activated by acidic treatment of the ceramic surface in the absence of a phosphate monomer. The two-bottle ceramic primer used in the present study consists of separate solutions of a phosphate monomer and a silane coupling agent (γ-MPS) in ethanol. Two versions were tested, one commercially available (TCP), and one, an experimental primer formulated without the inclusion of phosphate monomer (TCP-NoPM).

The results of the present study found that when no acid was applied to the silicon oxide ceramic surface, the microtensile bond strength (μTBS) of TCP was significantly higher than TCP-NoPM, and was ranked higher with respect to failure mode. This finding indicates that TCP-NoPM was not able to form a sufficient number of siloxane bonds with the ceramic surface, which suggests that γ-MPS was probably not activated. However, when the ceramic surface was treated with either phosphoric or hydrofluoric acid and then rinsed with water for 15 s, there were no significant differences in μTBS between the two ceramic primers and in the modes of specimen failure. In addition there were no significant differences in μTBS between the phosphoric and hydrofluoric acid treatments when the ceramic surface was rinsed for 15 s. On the other hand , SEM analysis revealed that when phosphoric acid was applied to the ceramic surface, there was little change in surface morphology compared to the untreated surface, whereas hydrofluoric acid created the typical lattice-like porous appearance. Therefore, in the case of TCP-NoPM, when phosphoric acid was applied to the ceramic surface, the significant improvement in μTBS must have resulted from improved chemical bonding at the resin-ceramic interface rather improved micromechanical retention, which would have been the case after hydrofluoric acid was applied.

SCHEM analysis of the ceramic surface revealed that a significant reduction in ceramic surface pH occurred when either phosphoric or hydrofluoric acid was applied and rinsed for 15 s, which indicates that an increase in the concentration of H^+ ions had occurred on the ceramic surface. Therefore, the significant improvement in the μTBS of TCP-NoPM after the application of phosphoric acid to the ceramic surface and rinsing for 15 s, was probably due to the activation of γ-MPS. We speculate that γ-MPS was activated by an increase in the concentration of H^+ ions on the ceramic surface. When the water rinsing time was increased from 15 s to 60 s, there was a significant increase in surface pH after both phosphoric and hydrofluoric acid treatment, indicating that there was a reduction in the concentration of H^+ ions on the ceramic surface. Moreover, while increasing the water rinsing time had no significant effect on the μTBS of the TCP groups, it led to a significant reduction in μTBS of the TCP-NoPM group after phosphoric acid treatment of the ceramic surface. These findings indicate that when the ceramic surface was treated with phosphoric acid, the μTBS of the TCP groups was not significantly affected by the change in surface pH because TCP contains phosphate monomer, which is sufficient to activate γ-MPS, regardless of the concentration of H^+ ions on the ceramic surface. On the otherhand, since TCP-NoPM does not contain phosphate monomer, γ-MPS could not have been activated. The number of activated γ-MPS molecules in TCP-NoPM might have been dependent upon the H^+ ion concentration after acid etching.

Regarding the effect of hydrofluoric acid, in the case of TCP, for each rinsing period, μTBS was not higher than the control group neither where there any differences in the failure modes. This finding is in agreement with the results of other researchers (Aida *et al.,* 1995). Although the SEM micrographs show a significant change in surface morphology after the application of hydrofluoric acid, this did not result in higher bond strengths in the TCP group. On the other hand, there were significant differences in μTBS among the TCP-NoPM groups treated with phosphoric and hydrofluoric acid and rinsed for 60 s. In the case of both phosphoric and hydrofluoric acid treatments, as the water rinsing time was increased from 15 s to 60 s, there were significant increases in surface pH. This indicates that a reduction in H^+ ion concentration had occurred on the ceramic surface. In the case of TCP-NoPM PA-60, the concentration of H^+ ions was probably not high enough to activate a sufficient number of γ-MPS molecules to form siloxane bonds, resulting in poor bonding between the resin and ceramic. On the other hand, the significantly higher μTBS of the TCP-NoPM HFA-60 group than the PA-60 group indicates that the reduction in chemical bonding was compensated for by an increase in micromechanical retention.

In conclusion, when phosphate monomer was present in the tested ceramic primer, treatment of the ceramic surface with either phosphoric or hydrofluoric acid did not significantly increase the bond strength of the tested dual-cure resin cement to silicon oxide ceramic. However, when no phosphate monomer was present in the ceramic primer, the bonding of dual cure resin cement to ceramic was significantly improved by acidic treatment of the ceramic surface. Acidic treatment of the ceramic surface and the duration of water rinsing altered the surface pH and there were significant differences in surface pH among the different water rinsing times for both acidic treatments. There were no significant differences in surface pH between phosphoric and hydrofluoric acid for each rinsing period. As water rinsing time increased, surface pH increased and the mTBS of the TCP-NoPM groups decreased, however, there were no significant changes in μTBS in the TCP groups. Acidic treatment of the silicon oxide ceramic surface probably increases the concentration of H^+ ions on the surface

, which when high enough, can activate γ-MPS when no phosphate monomer is present in the ceramic primer.

Chapter 5

General conclusions

Propelled by the increasing demand from both patients and clinicians for esthetically pleasing indirect restorations, dental manufacturers have introduced a wide array of both hybrid and all-ceramic restorative materials. When luting an indirect ceramic restoration containing silicon oxide, the creation of a micro-mechanically retentive surface through the application of hydrofluoric acid is considered necessary prior to applying a silane coupling agent and a resin cement. However, hydrofluoric acid is a hazardous substance and questions are being raised about whether hydrofluoric acid still has a place in the dental laboratory and clinic. Certainly, unless it is used in a very low concentration, it is not suitable for intra-oral use. This has led to the development of ceramic priming systems, which do not require the ceramic surface to be treated with hydrofluoric acid. The ability of a self-etching primer or dentin-bonding agent to function as a ceramic primer certainly simplifies the luting procedure. Dual-cure resin cement has become the preferred luting cement because it offers the advantages of controlled polymerisation and working time. However, research on the ability of this new generation of ceramic primers to bond dual-cure resin cement to ceramic has to date been limited. In particular, how factors such as light exposure, chemical versus dual-curing, chemical composition, long-term durability and acidic treatment of the ceramic surface might affect the dual-cure resin cement/ceramic bond.

Chapter 1

The aim of this investigation was to determine the microtensile bond strength and hardening of dual-cure resin cement when no light-exposure, light-exposurefrom one direction, and light-exposure from multiple directions were applied to different thicknesses of copy-milled ceramic treated with a ceramic primer. The results indicated that the direction of light source application has no significant effect on microtensile bond strength or resin hardness when the thickness of overlying restorative material is 2.0 mm or less. When greater than this value, use of multiple directed exposures demonstrated significantly better strength than when only one exposure duration was used. There were no significant differences in bond strength and microhardness when the 1 and 2 mm thick ceramic slices were light-cured for either 120 s from one direction, or for 20 s from six directions. However, when the thickness of the overlying ceramic was increased from 2 to 3 mm, a significant reduction in bond strength occurred when light-cure was applied for 120 s from one direction, but not when applied for 20 s each from six directions. These findings lead us to conclude that while the number of directions of light-exposure may not be so important in the case of a porcelain veneer, whose thickness is typically less than 1.5 mm, in the case of a large ceramic inlay or onlay, there may be regions of dual-cure resin cement below the ceramic restoration that are inaccessible to light. When there was no exposure to light, bond strength and hardness values of this group were among the lowest, which indicates that chemical-cure alone was not sufficient for the dual-cure resin cement to strongly bond to ceramic.

Chapter 2

It is important to evaluate the durability of the dual-cure resin cement ceramic bond, and so a study was undertaken to determine the effects of chemical-cure, exposure to light from one direction, and exposure to light from multiple directions, on the stability in water of the bond between dual-cure resin cement and a machinable ceramic treated with a multi-component ceramic primer. After priming with TCP, the bond strength of Bistite II significantly increased over time when exposed to light, whereas that of the no-light group significantly decreased over time. After priming with TCP, the bond strength of Panavia F increased over time, and after 6 weeks water storage, there were no significant differences between the no-light and light-exposed groups. Increases in bond strength were associated with increases in the number of cohesive failures in resin cement. After phosphoric acid treatment, priming with Liner Bond 2V/ Porcelain Bond Activator, and light exposure, the bond strength of Bistite II remained stable whereas that of Panavia F significantly reduced over time. These results indicate that the dual-cure resin cements differ in their ability to polymerize chemically and in the amount of light required for photo-initiated polymerization, which influences the durability of the dual-cure resin cement/ceramic bond. In addition, the resistance of the resin cement/ceramic bond to hydrolytic degradation appears to be dependent upon the chemical composition of the ceramic primer. The more hydrophilic is the ceramic primer, the poorer the stability of the dual-cure resin cement/ceramic bond.

Chapter 3

The findings of Chapter 2 indicated that a long-term durability study was necessary. And so, an investigation was undertaken to evaluate the microtensile bond strength of the dual-cure resin cement/silicon oxide ceramic bond after long-term immersion in water when the ceramic surface was treated with either a ceramic primer, a combination of primer and bonding resin or a ceramic bonding agent. After 1 day, there were no significant differences between Liner Bond 2V Primer/Porcelain Bond Activator (2V Pr), Liner Bond 2V Primer/ Porcelain Bond Activator and Liner Bond 2V Bond (2V Pr +Bd), and Photo Bond/Porcelain Bond Activator (P Bd), whereas after one year, significant differences were found. When the thickness of the overlying ceramic was 1 mm, the bond strength of Photo Bond after one year of water storage, was similar to that after one day. In both groups, the bond strength of 2V Pr and 2V Pr + Bd significantly decreased over time ($p<0.05$), which was accompanied by an increase in the percentage of complete adhesive failures. From these results it can be concluded that the chemical composition of the multi-component ceramic primer/bonding agent significantly affects the long-term durability of the dual-cure resin cement/silicon oxide ceramic bond. The presence of water in a ceramic primer has a significant detrimental effect on resin/ceramic bond durability. In addition, the thickness of the ceramic restoration influences dual-cure resin cement/ceramic bond durability.

Chapter 4

The action of ceramic primers in bonding dual-cure resin cement to ceramic is not fully understood. While it is accepted that the silane coupling agent must be hydrolysed before it can form siloxane bonds with a silicon dioxide ceramic surface, the role of the phosphate monomer in multicomponent ceramic primers is less clear. It is logical to assume that if an acidic substance is applied to the ceramic surface, there may be change in ceramic surface chemistry, in particular surface pH. Moreover, manufacturers of silicon oxide ceramic systems recommend hydrofluoric acid treatment of the ceramic surface, while manufacturers of ceramic primers do not. Some do however recommend phosphoric acid treatment, although the rational for this is unclear. Therefore a study was undertaken to examine the relationship between the ceramic primer and ceramic surface pH on the microtensile bond strength of dual-cure resin cement to silicon oxide ceramic. When no acid was applied to the ceramic surface, the microtensile bond strength of TCP was significantly higher than that of TCP without phosphate monomer. However, after treatment of the ceramic surface with either phosphoric or hydrofluoric acid, and 15s water rinsing, there was a significant reduction in surface pH, and no significant difference in bond strength between the two ceramic primers. For TCP, there were no significant differences in bond strength and failure mode between the control, phosphoric and hydrofluoric acid-treated groups when the water rinsing time was increased. Whereas, for TCP-NoPM and surface treatment with phosphoric acid, an increase in rinsing time resulted in a significant reduction in bond strength and a significant increase in surface pH. Acidic treatment of the ceramic surface did not significantly increase dual-cure resin/ceramic bond strengths when the ceramic primer, TCP, was used. Therefore, it is suggested that when no phosphate monomer is present in a ceramic primer, dual-cure resin cement/ceramic bond strength is dependent upon the concentration of H^+ ions on the ceramic surface.

The ideal all-ceramic primer has yet to be developed. The current generation of ceramic primers are able to strongly couple dual-cure resin cement to ceramic, which contains silicon dioxide. However, newer high strength alumina or zirconia ceramics do not contain a silicon dioxide phase and are therefore not suitable for priming with these particular ceramic primers (Wegner and Kern, 2000). Therefore, future ceramic primers should have the ability to couple resin cements to a wide range of ceramics irrespective of their composition.

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