Effect of Ceramic Surface Treatment on Tensile Bond Strength to a Resin Cement

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Purpose: The objective of this study was to test the following hypotheses: *(1)* hydrofluoric acid (HF)–treated ceramic surfaces produce the highest tensile bond strength to resin cements, independent of the ceramic microstructure and composition; and *(2)* the tensile bond strength test is appropriate for analysis of interfacial adhesion for ceramic-bonded-to-resin systems. **Materials and Methods:** Ceramic specimens were polished with 1-μm alumina abrasive and divided into four groups of 10 specimens for each of seven ceramic types. One of the following surface treatments was applied: *(1)* 10% ammonium bifluoride (ABF) for 1 minute; *(2)* 9.6% HF for 2 minutes; *(3)* 4% acidulated phosphate fluoride (APF) for 2 minutes; and *(4)* a silane coupling agent. The surface-treated areas were coated with an adhesive resin and bonded to a resin cement. Specimens were loaded to failure in tension using a testing machine. Tensile bond strength data were statistically analyzed, and fracture surfaces were examined to determine the mode of failure. **Results:** Silane-treated surfaces showed statistically higher mean tensile bond strength values than surfaces treated with any etchant (HF, ABF, APF). HF produced statistically higher mean tensile bond strengths than ABF and APF. All failures occurred in the adhesion zone. **Conclusion:** The tensile bond strength test is adequate for analysis of the adhesive zone of resin-ceramic systems. The chemical adhesion produced by silane promoted higher mean bond strength values than the micromechanical retention produced by any etchant for the resin-ceramic systems used in this study. *Int J Prosthodont 2002;15:248–253.*

The clinical success of indirect ceramic-bonded restorations and direct repaired ceramic prostheses relies on effective bonding to the ceramic surface.[1–3] The ceramic microstructure and composition have a significant effect on the fracture resistance of dentin-bonded ceramic crowns.[4] It has been shown that different surface topography is produced according to the type of etchant and the ceramic microstructure.[5–7] The ceramic surface irregularities produced by three etchants—hydrofluoric acid (HF), ammonium bifluoride (ABF), and acidulated phosphate fluoride (APF)—exhibit a unique pattern for each etching product. The most significant surface changes are produced by HF etching that preferentially attacks ceramic surface defects and the leucite phase.[7] Increasing the surface area by etching also promotes changes in the wetting behavior of porcelains,[8] which may also change the ceramic surface energy and its adhesive potential to resin.[9]

Materials and procedures used to cement ceramic restorations with luting resins are based on the results of bond strength tests that exhibit wide variability in fracture patterns. The commonly used shear bond test often produces fracture at a distance from the resin-ceramic adhesion zone that prevents measurement of interfacial bond strength, limits further improvements in bonding systems, and may lead to erroneous conclusions on bond quality.[3,10] In the search for a method that produces uniform stress distribution across the interface, investigators have evaluated similar adhesive systems under different bond test configurations.[10–12] These studies suggest that a tensile

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Table 1 Materials Used in the Study

Brand name (abbreviation)	Description (application time)	Manufacturer (lot No.)
Vitadur-α (VA)	Glass veneer; shade B4	Vita (3755)
Vitadur-N core (NC)	Alumina-reinforced ceramic; shade C4	Vita (591)
Vita Omega opaque (OO)	Opaque ceramic; shade B4	Vita (4054)
Vita Omega dentin (OD)	Leucite-based ceramic; shade B4	Vita (4144)
Fortress (MF)	Leucite-based ceramic; shade A2	Mirage (0211930509)
Mirage II Fiber (MII)	Zirconia-reinforced ceramic; shade A2	Mirage (692230)
Duceram LFC (LC)	Single-phase low-fusing ceramic; shade DA3.5	Ducera (026/8)
Porcelain Etching Gel (HF)	9.6% buffered HF (2 min)	Mirage
Porcelain Etchant (APF)	4% APF (2 min)	Mirage
Dicor Etching Gel (ABF)	10% ABF (1 min)	Dentsply
Ceramic primer (silane)	Coupling agent (γ-MPS) coat applied on ceramic surface	3M (20010213)
Scotchbond Multi-Purpose Plus (3.5 catalyst)	Applied with a brush on treated ceramic surface	3M (20010213)
RelyX (ARC)	Dual-cure luting resin cement	3M (20010316)

bond strength test may be more appropriate to evaluate the bond strength of adhesive interfaces because of more uniform interfacial stresses.

The objective of this study was to test the following hypotheses: *(1)* HF-treated ceramic surfaces produce the highest tensile bond strength to resin cements, independent of the ceramic microstructure and composition; and *(2)* the tensile bond strength test is adequate to evaluate the interfacial quality of ceramic-bonded-to-resin systems.

Materials and Methods

The materials used in this study are presented in Table 1. Forty specimen disks (diameter = 10 mm, height = 3 mm) of each ceramic were fabricated as previously described[7] and embedded in epoxy resin (Epofix Resin and Hardener, Struers, batch No. 0312-0333). All specimens (Fig 1) were polished using 240- through 1,200-grit SiC metallographic paper and finished with 1-µm polishing alumina (Mark V Laboratory). They were ultrasonically cleaned in distilled water for 10 minutes and dried. The ceramic surface was covered with a Teflon adhesive tape (Scotch, 3M, series #2-0300) containing a perforation of 3.7 mm in diameter in the center that limited the bonding area.

Four groups of 10 specimens each were selected at random from each of the seven ceramic types, and one of the surface treatments (HF, APF, ABF, silane) was applied to ceramic specimens in one of the groups.[7] The treated specimens were placed into the lower part of the outer metallic cylinder to rest against the lower jaw stops. A silicone rubber cylinder was placed under the embedded ceramic specimen and fixed in place with a securing pin to prevent any downward movement of the specimen during the bonding procedure. The unfilled resin 3.5 catalyst was applied

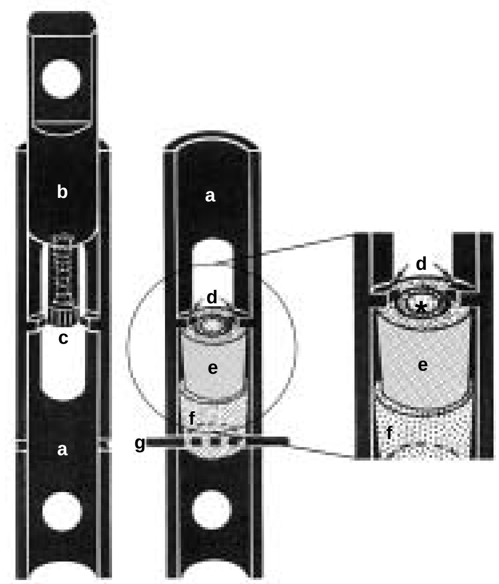

Fig 1 Tensile bond strength arrangement. Cross-section of outer metallic cylinder *(a)* fixed by the lower hole in the universal testing machine that prevents any bending movement of the metallic inner plunger *(b)*, which is also connected to the testing machine by the upper hole where the upward force is applied. The upper jaw *(c)* is screwed into the plunger and accommodates the resin cement. The lower jaw *(d)* stops the embedded ceramic disk specimen *(e)* from moving up during tensile loading. A silicone rubber cylinder *(f)* is placed under the embedded ceramic specimen and fixed in place with a securing pin *(g)* to prevent any downward movement of the specimen during the bonding procedure. * = bonding area on the ceramic disk.

with a brush to the bonding area on all treated ceramic specimens. A dual-cure resin cement was placed into the upper jaw in the metallic inner plunger. The plunger was placed into the upper part of the outer

Table 2 Ceramic Surface Treatments, Mean and Standard Deviation (SD) of Tensile Bond Strength (MPa), Duncan's Grouping (α = .05) for Each Ceramic Material, and Fracture Origin for All Experimental Groups*

Ceramic	Surface treatment	Mean	SD	Duncan's grouping†	Fracture origin (No. of specimens)
VA	HF	5.7	1.7	B	a (7); cc (3)
	ABF	3.6	0.8	C	a (10)
	APF	3.7	1.0	C	a (10)
	Silane	7.7	2.2	A	cc (10)
NC	HF	3.9	1.0	B	a (10)
	ABF	4.2	1.3	B	a (10)
	APF	3.9	1.1	B	a (10)
	Silane	9.8	2.7	A	cr (10)
OO	HF	4.6	1.2	B	a (10)
	ABF	3.2	0.5	B	a (10)
	APF	3.1	0.5	B	a (10)
	Silane	9.8	2.8	A	cc (5); cr (5)
OD	HF	5.6	1.2	AB	a (10)
	ABF	4.6	1.0	BC	a (10)
	APF	3.8	1.4	C	a (10)
	Silane	6.8	1.7	A	cc (3); cr (7)
MF	HF	7.7	1.8	B	a (3); cr (7)
	ABF	3.9	0.8	C	a (10)
	APF	3.9	0.7	C	a (10)
	Silane	11.4	3.5	A	cc (3); cr (7)
MII	HF	4.1	1.2	B	a (10)
	ABF	3.8	0.9	B	a (10)
	APF	3.0	0.5	B	a (10)
	Silane	11.1	3.2	A	cc (5); cr (5)
LC	HF	3.7	1.1	B	a (10)
	ABF	3.4	0.7	BC	a (10)
	APF	2.6	0.4	C	a (10)
	Silane	8.0	1.5	A	cc (10)

*n = 10 specimens per group.
†Duncan's statistical subsets for each ceramic; values with the same letters did not differ significantly (P < .05).
a = failure origin at the resin cement–ceramic interface; cc = failure origin within the ceramic adjacent to the adhesive interface; cr = failure origin within the resin adhesive.

metallic cylinder until the upper jaw containing the resin cement seated against the bonding area. The excess resin cement surrounding the upper jaw on the Teflon tape was removed with a brush. The load applied to the bonding area corresponded to the weight of the inner plunger (0.73 N). All bonded samples were stored for 24 hours at 37°C before determining tensile bond strength using an Instron universal testing instrument (model 1193, serial No. H2157) at a cross-head speed of 0.5 mm/min.

Tensile bond strength data were analyzed statistically using one-way analysis of variance (ANOVA) and Duncan's multiple-range test. Two-way ANOVA was also performed for each ceramic surface treatment (HF, APF, ABF, and silane) to investigate their influence on the bond strength to all ceramics.

Fracture surfaces were examined using light microscopy and scanning electron microscopy (SEM) to determine the mode of failure based on fracture origin, which was confirmed using X-ray dot mapping.[3] In preparation for the SEM (JSM 6400, Jeol) examination, the specimen fracture surfaces were sputter coated with gold-palladium for 3 minutes in a Hummer II Sputter Coater (21020, Technics) at a current of 10 mA and a vacuum of 130 mTorr.

Results

The mean tensile bond strength values ranged from 2.6 MPa for APF-treated LC ceramic to 11.4 MPa for silane-treated MF ceramic (Table 2). LC ceramic treated with any of the three etchants and bonded to resin produced the lowest mean bond strength values.

Treating the ceramic surface with the silane coupling agent produced statistically significantly higher mean tensile bond strength values than any etchant applied to any of the seven ceramic materials tested (Tables 2 and 3). Ceramics treated with either ABF or APF showed no statistically significant differences between mean bond strength values. Two-way ANOVA revealed that HF etching produced statistically significantly higher mean tensile bond strength values than the other two etchants (ABF and APF) for all ceramics (Table 3). These results correlate positively with the ceramic surface topography analysis presented in another study.[7]

SEM analysis, complemented by X-ray dot mapping, revealed that all fractures occurred within the "adhesion zone" (Fig 2). The adhesion zone is the region in which the adhesive interacts with the two substrates to promote bonding. More specifically, the adhesion zone in this study consisted of the following regions: *(1)* the interfacial region between the adhesive and the resin cement, within which molecular interaction and chemical bonding occurred between the two materials; *(2)* the adhesive; and *(3)* the interfacial region between the adhesive and the dental ceramic, including the surface region treated with the etchant or coated with silane to promote micromechanical or chemical bonding.[3]

Examination of the fracture surfaces showed no bulk fracture within either the resin cement or the dental ceramics. X-ray dot maps of these surfaces confirmed that they contained elements from the adhesive interfaces of the adhesion zone (Fig 2). These results suggest that the tensile bond strength configuration is adequate for analysis of the adhesive zone of the resin-ceramic systems used in this study.

Ceramic specimens treated with the silane coupling agent fractured in the adhesion zone either within the adhesive resin or within the ceramic. All ceramic specimens treated with ABF and APF etchants showed failure starting in the adhesive-ceramic interface. This failure was the predominant type for ceramic specimens treated with HF etchant (Tables 2 and 3).

Table 3 Ceramic Surface Treatments, Mean Tensile Bond Strength Values for Seven Ceramics Using the Same Surface Treatment (n = 70), Duncan's Grouping (α = .05), and Fracture Origin for the Ceramic Treatments

Surface treatment	Mean (MPa)	Duncan's grouping*	Fracture origin (No. of specimens)
HF	5.0	B	a (60); cr (7); cc (3)
ABF	3.8	C	a (70)
APF	3.4	C	a (70)
Silane	9.2	A	cc (36); cr (34)

*Duncan's statistical subsets; values with the same letters did not differ significantly (*P* < .05).
a = failure origin at the resin cement–ceramic interface; cr = failure origin within the resin adhesive; cc = failure origin within the ceramic adjacent to the adhesive interface.

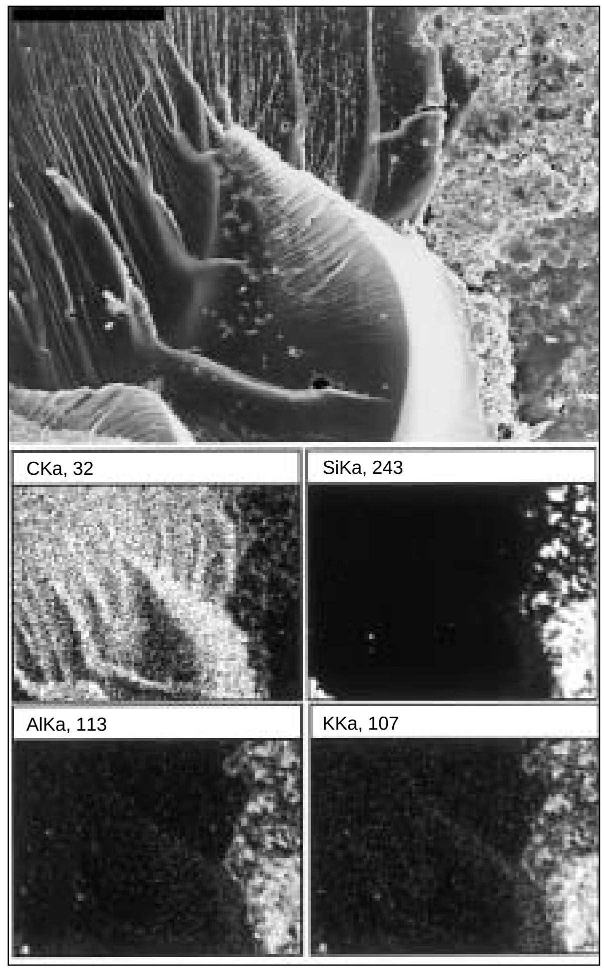

Fig 2 SEM view *(top)* and X-ray elemental maps of fracture surface of HF-treated MF ceramic bonded to resin cement. The labels at the top of X-ray maps indicate the elements and their intensity. The *left center* map (CKa, 32) shows the carbon intensity on the adhesive layer. The other three maps show the ceramic surface. Note that the adhesion zone fracture starts along the ceramic-adhesive interface by crack formation *(bottom right)* and propagates into the adhesive resin (bar = 100 µm; original magnification × 300).

Discussion

Restorative dentistry in general has recently focused on esthetics and adhesion applications where most of the manufacturers and practitioners, and even some researchers, tend to look for products that offer the "highest" bond strength values. Clinical long-term trials should be the ultimate test to justify a new product. However, they are costly and time consuming, and manufacturers are not obliged to carry out such studies prior to launching a new product. Therefore, laboratory bond strength test data are most frequently used to demonstrate the quality of the bond. The data are usually obtained using either shear or tensile bond strength tests. Several scientists have shown the problems associated with most popular test arrangements used in dentistry today, questioning the reliability of such measurements to provide useful information relevant to clinical adhesive behavior.[10,13–19] Therefore, the challenge of designing an adequate standardized bonding test remains.[20–22]

Several studies have identified the nonuniform stress distributions along bonded interfaces. These variable stress patterns suggest that a standardized research protocol may address only part of the problem.

The nonuniform interfacial stress distribution generated for conventional tensile and shear bond strength tests initiates fractures from flaws at the interface or in the substrate in areas of high stress concentration. These studies also suggest that a tensile bond strength test may be more appropriate to evaluate the bond strength of adhesive interfaces because of more uniform interfacial stresses.[3,10,13–15,23–26]

The basic principle of a tensile bond strength test is to measure the strength of the bonding area between two substrates by pulling them apart. A load/displacement curve, which is converted to a nominal stress/nominal strain ($\sigma n/\epsilon n$) curve, is generated during normal tensile testing. This plotting method allows comparison of data for specimens having different (although standardized) sizes and areas and examination of the properties of a material, unaffected by specimen size. The advantage of keeping the stress in nominal units is that the onset of necking can clearly be seen on the $\sigma n/\epsilon n$ curve. This principle does not quite work for tensile bond strength tests, where the bonding area is formed by a thin layer of composite or polymer material supposedly bonded to the substrates by micromechanical retention, molecular entanglement, physical or chemical adhesion, or even a combination of these mechanisms. In addition, defects (cracks, voids, inadequate surface conditions) within this layer, specimen geometry, and different research/test protocols lead to different results.[10,13,27] Nevertheless, the major difficulty of this type of test is to maintain the alignment during both bonding and testing to avoid stress concentrations because of incorrect interfacial geometry and bending movement.[3,26]

The tensile bond strength configuration used in this study prevents these difficulties because *(1)* the outer metallic cylinder has its lower end fixed to the testing machine; and *(2)* it is designed to guide the upper jaw straight down during the bonding procedure and straight up during tensile loading. Therefore, the outer cylinder keeps the inner complex containing the bonded specimen aligned, reducing the occurrence of stress concentrations because of test design geometry. Yet, stress concentrations can also occur because of geometric discontinuities, stress concentrators such as cracks, and differences in elastic moduli of the specimen components.

A careful interpretation of the failure mode is required to prevent inappropriate conclusions about the utility of any bond strength test configuration. In addition, an understanding of the fracture mechanics concepts and the analysis of fracture events on the basis of fractography will reduce the risk for data misinterpretation, such as the inference that the bond strength must exceed the cohesive strength of the porcelain when the fracture initiates away from the interface.[3,28,29]

Fractographic analysis has shown that the weak link in the adhesion of ceramic to either tooth structure or restorative composite material is the ceramic-resin interface.[1–3] This observation was confirmed by the results of the present study, since all fracture origins were located in the adhesion zone at the resin cement–ceramic interface (a), within the resin adhesive (cr), or within the ceramic (cc). The interfacial failures (a) started by crack formation within the remaining glassy phase that was weakened by the etching process. This weakening effect of etchants on the ceramic surface layer is probably caused by their preferential attack of crystal boundaries.[3,7] No interfacial fracture was observed when silane was the only ceramic surface treatment applied. This observation, along with the results of the tensile bond strength test, suggests that the chemical bond promoted by the silane coupling agent is the major mechanism responsible for the adhesion of resin-ceramic systems. This mechanism has also been proposed in other studies.[3,6,30]

As previously reported, different ceramic topography is produced according to the type of etchant and the ceramic microstructure, with HF producing the most aggressive etching pattern on all dental ceramics examined.[5,7] This highly irregular HF-treated ceramic surface produced significantly higher mean bond strength values than the other two etchant-treated ceramic surfaces. In addition, the lowest and highest mean bond strength values for etched samples were 2.6 MPa for APF-treated LC ceramic and 7.7 MPa for HF-treated MF ceramic, respectively. These results correlate positively with the etching patterns produced by each etchant on different ceramic microstructures.[7] These results suggest that the weakening effect caused by etching of the ceramic surface can be minimized by a highly micromechanical retentive surface that favors bonding to the adhesive resin.

This study showed that HF-etched ceramic surfaces bonded to a resin cement produced higher mean bond strength values than the other two etchant-treated ceramic surfaces (ABF and APF). Overall, the silane-treated ceramics showed the highest mean bond strength values, indicating the major contribution of this ceramic surface treatment on bonding to resin. As fracture always occurred in the adhesion zone, the tensile bond strength test design presented in this study appears to be adequate to test the bond strength of resin-ceramic systems.

Acknowledgments

This study was partially supported by Capes do Brazil and NIH-NIDCR grant DE06672. The authors thank Dr C. Shen for performing the statistical analysis. We also thank 3M Dental Products, Mirage Dental Products, and Vita Zahnfabrik for providing some of the materials used in this study.

References

1. Burke FJ, Watts DC. Effect of differing resin luting systems on fracture resistance of teeth restored with dentin-bonded crowns. Quintessence Int 1998;29:21–27.
2. Chang JC, Nguyen T, Duong JH, Ladd GD. Tensile bond strengths of dual-cured cements between a glass-ceramic and enamel. J Prosthet Dent 1998;79:503–507.
3. Della Bona A, Anusavice KJ, Shen C. Microtensile strength of composite bonded to hot-pressed ceramics. J Adhesive Dent 2000;2: 305–313.
4. Mak M, Qualtrough AJ, Burke FJ. The effect of different ceramic materials on the fracture resistance of dentin-bonded crowns. Quintessence Int 1997;28:197–203.
5. Della Bona A, van Noort R. Ceramic surface preparations for resin bonding. Am J Dent 1998;11:276–280.
6. Jardel V, Degrange M, Picard B, Derrien G. Correlation of topography to bond strength of etched ceramic. Int J Prosthodont 1999; 12:59–64.
7. Della Bona A, Anusavice KJ. Microstructure, composition, and etching topography analyses of dental ceramics. Int J Prosthodont 2002; 15:159–167.
8. Phoenix RD, Shen C. Characterization of treated porcelain surfaces via dynamic contact angle analysis. Int J Prosthodont 1995;8: 187–194.
9. Jardel V, Degrange M, Picard B, Derrien G. Surface energy of etched ceramic. Int J Prosthodont 1999;12:415–418.
10. Della Bona A, van Noort R. Shear versus tensile bond strength of resin composite bonded to ceramic. J Dent Res 1995;74: 1591–1596.
11. Kitasako Y, Burrow MF, Nikaido T, et al. Shear and tensile bond testing for resin cement evaluation. Dent Mater 1995;11:298–304.
12. Cardoso PEC, Braga RR, Carrilho MRO. Evaluation of micro-tensile, shear and tensile tests determining the bond strength of three adhesive systems. Dent Mater 1998;14:394–398.
13. van Noort R, Cardew GE, Howard IC, Noroozi S. The effect of local interfacial geometry on the measurement of the tensile bond strength to dentin. J Dent Res 1991;70:889–893.
14. van Noort R, Noroozi S, Howard IC, Cardew G. A critique of bond strength measurements. J Dent 1989;17:61–67.
15. Versluis A, Tantbirojn D, Douglas WH. Why do shear bond tests pull out dentin? J Dent Res 1997;76:1298–1307.
23. Chadwick RG, Mason AG, Sharp W. Attempted evaluation of three porcelain repair systems—What are we really testing? J Oral Rehabil 1998;25:610–615.
24. Degrange M, Charrier JL, Attal JP, Asmussen E. Bonding of luting materials for resin-bonded bridges: Clinical relevance of in vitro tests. J Dent 1994;22(suppl 1):28–32.
25. Pashley DH, Sano H, Ciucchi B, Yoshiyama M , Carvalho RM. Adhesion testing of dentin bonding agents: A review. Dent Mater 1995;11:117–125.
26. Sudsangiam S, van Noort R. Do dentin bond strength tests serve a useful purpose? J Adhesive Dent 1999;1:57–67.
16. Anusavice KJ, Dehoff PH, Fairhurst CW. Comparative evaluation of ceramic-metal bond tests using finite element stress analysis. J Dent Res 1980;59:608–613.
17. Anusavice KJ. Screening tests for metal-ceramic systems. In: McLean JW (ed). Dental Ceramics: Proceedings of the First International Symposium on Ceramics. Chicago: Quintessence, 1983:371–414.
18. Ban S, Anusavice KJ. Influence of test method on failure stress of brittle dental materials. J Dent Res 1990;69:1791–1799.
19. DeHoff PH, Anusavice KJ, Wang Z. Three-dimensional finite element analysis of the shear bond test. Dent Mater 1995;11:126–131.
20. Stanley HR. An urgent plea for a standardized bonding (adhesion) test [guest editorial]. J Dent Res 1993;72:1362–1363.
21. International Standards Organization. ISO/TR 11405 Dental Materials—Guidance on Testing of Adhesion to Tooth Structure. Geneva: ISO, 1994.
22. Sheriff M. Dental materials 1991 literature review: Adhesion and mechanisms. J Dent 1993;21:10–11.
27. Anusavice KJ, Hojjatie B. Tensile stress in glass-ceramic crowns: Effect of flaws and cement voids. Int J Prosthodont 1992;5:351–358.
28. Mecholsky JJ Jr. Fracture mechanics principles. Dent Mater 1995; 11:111–112.
29. Tantbirojn D, Cheng YS, Versluis A, Hodges JS, Douglas WH. Nominal shear or fracture mechanics in the assessment of composite-dentin adhesion? J Dent Res 2000;79:41–48.
30. Chen JH, Matsumura H, Atsuta M. Effect of etchant, etching period, and silane priming on bond strength to porcelain of composite resin. Oper Dent 1998;23:250–257.