Self-Etching Resin Adhesives

Howard E. Strassler, DMD

The Holy Grail for adhesion to enamel and dentin has been described as being a single component, no-mix adhesive that can be applied directly to enamel and dentin for the purpose of bonding any restorative material to tooth structure. While this product does not yet exist, the manufacturers and researchers are hard at work developing and evaluating improved bonding systems. The introduction of self-etch adhesive systems has been an important step in achieving this goal of an all-in-one bonding agent.

The idea of adhesive bonding to dentin was postulated more than 50 years ago as involving a potential chemical bond between the methacrylate group of resins to the collagen surface of dentin.[1] In 1955, Buonocore described a clinical technique that used a diluted phosphoric acid to etch the enamel surface and provide for retention of unfilled, self-cured acrylic resins.[2] The resin would mechanically lock to the microscopically roughened enamel surface, forming small "tags" as it flowed into the 10-µm to 40-µm deep enamel microporosities and then polymerized. The first clinical use of this technique was the placement of sealants.[3] The combination of acid-etching enamel and adhesive composite resin restorations afforded the benefits of reduction or elimination of microleakage at the enamel margins, less discoloration at the margins, lower rates of recurrent caries, and improved retention of the restoration.[4,5]

The effectiveness and success of the etched enamel/resin bond has been demonstrated in many reported clinical trials.[6] Unlike enamel bonding, dentin bonding has seen an evolution in its viability. Effective dentin-bonding materials should fulfill the following goals:

- The material should be retentive to dentin at a clinically acceptable level, and should be able to withstand intraoral forces of occlusion and mastication.
- The bond should be instantaneous once the material has set.
- The material and technique must be biocompatible.
- The material should resist the forces of polymerization shrinkage of composite resins and the coefficient of thermal expansion and contraction to eliminate microleakage.
- The material should create a long-lasting bond to dentin.
- Postoperative sensitivity must be minimized or eliminated.

In 1956, the earliest research with dentin bonding focused on chemical adhesion of resins to the inorganic components of dentin. Buonocore and coworkers developed a methacrylate-based dentin adhesive that contained phosphate groups to attach to the calcium ions on the dentin surface.[7] The basis of the bond was the presence of the dentin smear layer.[8] While a weak bond was created, unfortunately it was a clinically unacceptable bond to dentin. This basis of a phosphate-calcium bond later became the third-generation phosphate-ester bonding systems. These bonding systems, eg, the original Scotchbond™ (3M ESPE, St. Paul, MN) and BondLite (Sybron Dental Specialties, Inc, Orange, CA) among others, bonded to the calcium-rich dentin smear layer and to etched enamel. Their bond strengths to dentin were limited by the bond of the smear layer to the dentin. Unfortunately, the durability of the bond was impacted by hydrolysis that occurred over time to the phosphate/calcium bond.[9,10] These products had limited success and the search for a better adhesive to dentin continued.

At the same time, another research path for dentin bonding investigated the use of a total-etch approach, etching the enamel and dentin simultaneously.[11,12] At the time, there was concern that phosphoric acid placed on dentin would cause pulpal inflammation and necrosis.[13] Jennings and Ranly demonstrated that the pulpal effect of phosphoric acid on dentin for 1 minute was minimal.[14] Early results reported on dentin etching were disappointing because the adhesive resin used was the same unfilled, hydrophobic Bis-GMA bonding resin used for etched enamel.[12] The hydrophobic resin would not wet the moist, vital dentin and predictable adhesion could not be produced. The breakthrough in the total-etch approach was first described in the late 1970s by Fusayama and coworkers,[15] Bertolotti,[16] and Kanca.[17] They demonstrated the success of the total-etch adhesive bond based on the addition of a hydrophilic monomer, usually hydroxyethyl methylmethacrylate to the primer and adhesive. This monomer allows the adhesive resin to penetrate the peritubular dentin and dentinal tubules.[18]

These concepts led to the development of multi-step adhesive bonding systems, which required the application of a primer and then an adhesive resin, in the late 1980s and early 1990s that used a total-etch technique with phosphoric acid. In the mid 1990s clinicians sought a simplified approach that used fewer steps for adhesive placement. Manufacturers responded with the introduction of single-bottle primer/adhesive total-etch bonding systems. With these two different classes of bonding systems came the classification and description of bonding systems based on generational timeline changes. Fourth-generation bonding systems referred to total-etch, multi-bottle (multi-step) systems and fifth-generation systems were total-etch, single-bottle bonding agents that contained both primer and adhesive. Both fourth- and fifth-generation products required a total-etch with phosphoric acid before adhesive placement.

Simplification of technique and a reduction in the number of steps was desired. It was obvious that the more steps that were

required to bond a restoration, the greater the potential for inconsistency in the timing of application, rinsing, drying, rewetting dentin, and maintaining a controlled operative field during treatment. This inconsistency has an impact on the success of the bond and the durability of the restoration. Manufacturers responded by placing research efforts in the development of self-etching adhesive systems.[1]

Many manufacturers have referred to self-etch adhesives as either sixth- or seventh-generation adhesive systems. In this author's view, the description of adhesives based on a generational view can be confusing. Christensen described a classification system for bonding agents based on the components used to achieve adhesion to dentin and enamel.[19] He divided adhesives into two main categories—total-etch (TE) and self-etch (SE). Within each category he then subdivided the classifications based on the number of reagents that were used for the adhesive technique. This classification system is listed in Table 1 with examples in each classification. Table 2 lists recommendations for the clinical applications of the two types of adhesive systems listed based on the clinical evidence.

Currently, the clinician has the choice between two different approaches for bonding that have different mechanisms in how they interact with the dentin smear layer: a TE approach or a SE approach.[20] The TE technique uses 30% to 40% phosphoric acid, which removes the dentin smear layer. The phosphoric acid is rinsed with water and dried from the dentin. The dentin is then rewetted with water, leaving a damp surface; an adhesive resin is then applied.

The introduction of a SE adhesive simplifies the bonding process. The SE approach does not require a separate etching step because the etchant is incorporated into the adhesive (either in a separate self-etching primer or in the adhesive itself). Also, a separate step of rewetting with water is eliminated because SE adhesives contain water and are never completely dried from the tooth. SE adhesives do not remove the smear layer but incorporate it into the adhesive. Their compositions are aqueous mixtures of acidic functional monomers, usually phosphoric acid esters, with a pH value higher than phosphoric acid (TE type) gels.[21] It has been reported that the pH of Clearfil® SE Bond (Kuraray America, Inc, New York, NY) is approximately 2.0, compared to a pH of 0.5 to 1.0 for typical phosphoric acid gels.[22]

SELF-ETCHING ADHESIVES

As stated previously, there has always been concern for contamination and inconsistency with multiple-step bonding systems. In response to this concern, self-etching adhesive systems have been developed. Recent research has investigated self-etching adhesive systems. A chief complaint among practitioners with composite resin restorations has been the rate of postoperative sensitivity especially when using TE bonding after the placement of Class 1, 2, and 5 restorations. Several different studies evaluated postoperative sensitivity using both TE and SE adhesives.[19,23-26] The

Table 1: Adhesive System Classification with Partial Listing of Products*

Total-Etch Adhesives

Multiple Bottle

Syntac®	Ivoclar Vivadent
Tenure® MP	Den-Mat Corporation
Gluma® Solid Bond	Heraeus Kulzer
Scotchbond™ MP	3M ESPE
ProBond®	DENTSPLY
Optibond® FL	Kerr Corporation
DenTASTIC®	Pulpdent Corporation

Single Bottle

Prime & Bond® NT™	DENTSPLY
Adper™ Single Bond Plus	3M ESPE
Excite®	Ivoclar Vivadent
Gluma® Comfort Bond	Heraeus Kulzer
Syntac® Single Component	Ivoclar Vivadent
Optibond® Solo Plus	Kerr Corporation
DenTASTIC® Uno™	Pulpdent Corporation
One Coat® Bond	Coltène/Whaledent
Tenure® Quick	Den-Mat Corporation

Self-Etching Adhesives

Multiple Step

Clearfil® Liner Bond 2V	Kuraray America
Clearfil® SE Bond	Kuraray America
Clearfil® DC Bond	Kuraray America
Tyrian™ SPE	Bisco
Simplicity™	Apex Dental Materials

Single-Step Mix Systems

AdheSE®	Ivoclar Vivadent
Prompt™ L-Pop™	3M ESPE
Touch&Bond®	Parkell
One-Up Bond F Plus	J. Morita USA
Tenure® Unibond	Den-Mat Corporation

No-Mix Systems

iBond™	Heraeus Kulzer
GC G-Bond™	GC America
Optibond® All-in-One	Kerr Corporation
Xeno® IV	DENTSPLY
Clearfil® S^3	Kuraray America

**Check with manufacturer for those products that can be used with self- and dual-cure composite resins.*

Table 3: Advantages of Self-Etching Adhesive Systems

- Contains water (hydrates dentin collagen)
- Wet bonding is incorporated into the self-etching adhesive
- Fewer components
- Fewer clinical steps
- May minimize potential for postoperative sensitivity

Figure 1A Class 2 carious lesion on the distal surface of the mandibular second premolar.

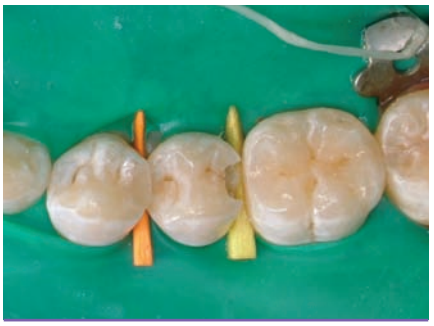

Figure 1B Class 2 cavity preparation.

Figure 1C Restoration using a self-etch adhesive with a micromatrix hybrid composite resin.

Figure 2A Class 3 carious lesion on the mesial surface of the maxillary lateral incisor.

Figure 2B Class 3 and lingual cavity preparations.

Figure 2C Restorations using a self-etch adhesive with a microfill hybrid composite resin.

Clearfil® Liner Bond 2 (Kuraray America, Inc) Class 1 through Class 5 restorations were evaluated. At the 10-year recall, 90.9% of the restorations exhibited some marginal breakdown and 88.6% of the restorations had marginal staining. The retention rate of the restorations for those prepared cavity preparations and restorations with the SE was 100% at each recall period (50.5% at 10 years or the original placed restorations). This SE system was an acceptable adhesive for restoring prepared teeth.[50] Swift and coworkers compared a TE (Optibond® Solo Plus, Kerr Corporation, Orange, CA) to a SE (Xeno® III, DENTSPLY Caulk, Milford, DE) for sensitivity and found that for both adhesives, 23% of the treated teeth had short-duration sensitivity to biting pressure that resolved after 10 days.[51] A 24-month clinical trial with a two-step SE (Clearfil Protect Bond) and a one-step SE (Xeno III) for NCCL demonstrated retention rates of over 96% with no postoperative sensitivity at the 2-year recall. Compared to 3% of the Clearfil Protect Bond, 12% of the Xeno III restorations had marginal staining.[52] In an 18-month study with Clearfil SE Bond, enamel beveling or acid-etching did not improve the retention rate of NCCL restored lesions. The retention rate for the four groups tested was 100%.[53] A 5-year clinical evaluation of One-Up Bond F Plus (J. Morita USA, Inc, Irvine, CA) with 42.5% of the original restorations recalled showed a 92% retention rate, with 48% of the restorations demonstrating marginal staining.[54] Other studies have demonstrated similar results with SE systems to those previously cited.[55-63] Retention with SE adhesive systems is not a problem and there are minor rates of marginal staining. Figure 1A through Figure 2C demonstrate two cases restored using SE adhesive systems.

An area of recent investigation has been the compatibility of TE and SE systems with composite resin cementation. There is contradictory evidence that some single-bottle adhesive systems do not bond well to self-cure and dual-cure composite resins because of the acidity of the single-bottle primer-adhesive. Studies demonstrating a decreased bond and other studies showing no effect have been reported.[64-66] Some recent studies evaluating SE systems and compatibility with dual-cure and self-cure composite resins have demonstrated some changes in chemistry that have resulted in composite resin–adhesive incompatibility.[67,68] This variance requires that the clinician review the manufacturer's recommendations for use with self-cure and dual-cure composite resins.

CONCLUSION

Clinicians have seen multiple generations of adhesive systems in the last 20 years. Many of these bonding systems have required multiple steps to include etching with phosphoric acid, rinsing with an air-water spray, drying, rewetting the preparation, applying the primer, drying, applying the adhesive resin,

and light-curing. Based on the current clinical evidence and the recommendations of manufacturers, SE adhesive systems can be used successfully for the restoration of Classes 1, 2, 3, and 5 preparations. SE adhesives provide adequate enamel etching to resist microleakage and marginal staining and adequate retention of both prepared teeth and NCCL Class 5 restorations.

With the introduction of clinically reliable self-etching bonding systems for use in the restoration of routine tooth preparations, the practitioner can place restorations in a more simplified manner. SE systems are different from the bonding systems previously used and the manufacturers' recommendations must be followed to ensure clinical success.

DISCLOSURE

The author has received honorarium or grant/research support from 3M ESPE, Bisco, Den-Mat, DENTSPLY, GC America, Heraeus Kulzer, Pulpdent, and Ultradent.

REFERENCES

1. Leinfelder KF, Kurdziolek SM. Self-etching bonding agents. *Compend Contin Educ Dent.* 2003;24(6):447-456.
2. Buonocore MG. A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res.* 1955; 34(6):849-853.
3. Cueto EI, Buonocore MG. Sealing of pits and fissures with an adhesive resin: its use in caries prevention. *J Am Dent Assoc.* 1967;75 (1):121-128.
4. Torney DL, Denehy GE, Teixeira LD. The acid etch class III composite resin restoration. *J Prosthet Dent.* 1977;38(6):623-626.
5. Jordan RE, Suzuki M, Gwinnett AJ, et al. Restoration of fractured and hypoplastic incisors by the acid etch resin technique: a three year report. *J Am Dent Assoc.* 1977;95(4):795-803.
6. Strassler HE. Applications of total-etch adhesive bonding. *Compend Contin Educ Dent.* 2003;24(6):427-436.
7. Brudevold F, Buonocore M, Wileman W. A report on a resin capable of bonding to human dentin surfaces. *J Dent Res.* 1956;35:846-851.
8. Diamond A, Carrel R. The smear layer: a review of restorative progress. *J Pedod.* 1984;8(3):219-226.
9. Retief DH, Gross JD, Bradley EL, et al. Tensile bond strengths of dentin bonding agents to dentin. *Dent Mater.* 1986;2(2):72-77.
10. Eliades GC, Caputo AA, Vougionklakis GJ. Composition, wetting properties and bond strength with dentin of 6 new dentin adhesives. *Dent Mater.* 1985;1(5):170-176.
11. Lee HL, Orlowski JA, Scheidt GC, et al. Effects of acid etchants on dentin. *J Dent Res.* 1973;52(6):1228-1233.
12. Torney DL. The retentive ability of acid-etched dentin. *J Prosthet Dent.* 1978;3(2):169-172.
13. Skinner EW, Phillips RW. *The Science of Dental Materials.* 5th ed. Philadelphia, PA: WB Saunders Company; 1960;277.
14. Jennings RE, Ranly DM. Autoradiographic studies of P32 penetration into enamel and dentin during acid etching. *ASDC J Dent Child.* 1972;39(1):69-71.
15. Fusayama T, Nakamura M, Kurosaki N, et al. Non-pressure adhesion of a new adhesive restorative system. *J Dent Res.* 1979;58:1364-1370.
16. Bertolotti RL. Acid etching of dentin. *Quintessence Int.* 1990;21:77-78.
17. Kanca J III. One-year evaluation of a dentin-enamel bonding system. *J Esthet Dent.* 1990;2(4):100-103.
18. van Meerbeek B, Inoue S, Perdigao J, et al. Enamel and dentin adhesion. In: *Fundamentals of Operative Dentistry a Contemporary Approach.* 2nd edition. Summitt JB, Robbins JW, Schwartz RS, eds. Hanover Park, IL: Quintessence Books, 2001;178-235.
19. Christensen G. Update on adhesive systems. *CRA Newsletter.* 2002;26(6)2.
20. Perdigao J, Geraldeli S, Hodges JS. Total-etch versus self-etch adhesive effect on postoperative sensitivity. *J Am Dent Assoc.* 2003;134 (12):1621-1629.
21. Tay FR, Sano H, Carvalho R, et al. An ultrastructural study of the influence of acidity on self-etching primers and smear layer thickness on bonding to intact dentin. *J Adhes Dent.* 2000;2(2):83-98.
22. Perdigao J, Lambrechts P, van Meerbeek B, et al. Morphological field emissions- SEM study of the effect of six phosphoric acid etching agents on human dentin. *Dent Mater*. 1996;12(4):262-271.
23. Akpata ES, Behbehani J. Effect of bonding systems on post-operative sensitivity from posterior composites. *Am J Dent.* 2006;19(3): 151-154.
24. Perdigao J, Anauate-Netto C, Carmo AR, et al. The effect of adhesive and flowable composite on postoperative sensitivity: 2-week results. *Quintessence Int.* 2004;35(10):777-784.
25. Unemori M, Matsuya Y, Akashi A, et al. Self-etching adhesives and postoperative sensitivity. *Am J Dent.* 2004;17(3):191-195.
26. Browning WD, Myers M, Downey M, et al. Reduction in post-operative sensitivity: a community based study. *J Dent Res.* 2006;85 (Special Issue B): Abstract #1151.
27. Miller MB. Self-etching adhesives: solving the sensitivity conundrum. *Pract Proced Aesthet Dent.* 2002;14(5):406.
28. Lee R, Blank JT. Simplify bonding with a single step: one component, no mixing. *Contemporary Esthetics and Restorative Practice.* 2003; 7(5):45-46.
29. Santini A, Ivanovic V, Ibbetson R, et al. Influence of cavity configuration on microleakage around Class V restorations bonded with seven self-etching adhesives. *J Esthet Restor Dent.* 2004;16(2):128-136.
30. Kanca J. Improving bond strength through acid etching of dentin and bonding to wet dentin surfaces. *J Am Dent Assoc.* 1996;123(9):35-43.
31. Gwinnett AJ. Moist versus dry dentin: it effect on shear bond strength. *Am J Dent.* 1992;5(3):127-129.
32. Finger WJ, Tani C. Effect of relative humidity on bond strength of self-etching adhesives to dentin. *J Adhes Dent.* 2002;4(4):277-282.
33. Turkun M, Turkun LS, Kalender A. Effect of cavity disinfectants on the sealing ability of nonrinsing dentin-bonding resins. *Quintessence Int.* 2004;35(6):469-476.

34. Elkhatib H, Nakajima M, Hiraishi N, et al. Surface pH and bond strength of a self-etching primer/adhesive system to intracoronal dentin after application of hydrogen peroxide bleach with sodium perborate. *Oper Dent.* 2003;28(5):591-597.
35. Perdigao J, Geraldeli S. Bonding characteristics of self-etching adhesives to intact versus prepared enamel. *J Esthet Restor Dent.* 2003:5:32-42.
36. Brackett WW, Ito S, Nishitani Y, et al. The microtensile bond strength of self-etching adhesives to ground enamel. *Oper Dent.* 2006;31 (3):332-337.
37. Di Hipolita V, de Goes MF, Carrilho MR, et al. SEM evaluation of contemporary self-etching primers applied to ground and unground enamel. *J Adhes Dent.* 2005;7(3):203-211.
38. Aljubouri YD, Millette DT, Gilmour WH. Six and 12 months' evaluation of a self-etching primer versus two-stage etch and prime for orthodontic bonding: a randomized clinical trial. *Eur J Orthod.* 2004;26(6):565-571.
39. Murfitt PG, Quick AN, Swain MV, Herbison GP. A randomised clinical trial to investigate bond failure rates using a self-etching primer. *Eur J Orthod.* 2006;28(5):444-449.
40. House K, Ireland AJ, Sherriff M. An investigation into the use of a single component self-etching primer adhesive system for orthodontic bonding: a randomized controlled clinical trial. *J Orthod.* 2006;33: 38-44.
41. Kiremiti A, Yalcin F, Gokalp S. Bonding to enamel and dentin using self-etching adhesive systems. *Quintessence Int.* 2004;35(4):367-370.
42. Tay FR, Pashley DH, King NM, et al. Aggressiveness of self-etch adhesives on unground enamel. *Oper Dent.* 2004;29(3):309-316.
43. Lopes GC, Marson FC, Vieira LC, et al. Composite bond strength to enamel with self-etching primers. *Oper Dent.* 2004;29(4):424-429.
44. Perdigao J, Gomes G, Lopes MM. Influence of conditioning time on enamel adhesion. *Quintessence Int.* 2006;37(1):35-41.
45. Christensen G. Self-etch primer (SEP) adhesives update. *CRA Newsletter.* 2003;2(11/12):1-5.
46. van Meerbeek B, DeMunck J, Mattar D, et al. Microtensile bond strengths of an etch and rinse and self-etch adhesive to enamel and dentin as a function of surface treatment. *Oper Dent.* 2003;28 (5):647-660.
47. Shimada Y, Iwamoto N, Kawashima M, et al. Shear bond strength of current adhesive systems to enamel, dentin, and dentin-enamel junction region. *Oper Dent.* 2003;28(5):585-590.
48. Senawongse P, Sattabanasuk V, Shimada Y, et al. Bond strengths of current adhesive systems on intact and ground enamel. *J Esthet Restor Dent.* 2004;16(2):107-116.
49. Tani C, Finger WJ. Effect of smear layer thickness on bond strength mediated by three all-in-one self-etching priming adhesives. *J Adhes Dent.* 2002;4(4):283-289.
50. Akimoto N. Ten-year clinical evaluation of self-etching primer system. *J Dent Res.* 2004;83(Special Issue A): Abstract #249.
51. Swift EJ Jr, Heymann HO, Pereira PNF, et al. Clinical evaluation of a two-component self-etching adhesive and hybrid composite. *J Dent Res.* 2005;84(Special Issue A): Abstract #1780.
52. Turkun LS. 24-month clinical performance of two self-etching adhesive systems. *J Dent Res.* 2005;84(Special Issue A): Abstract #1782.
53. Anauate-Netto C, Carmo AR, Perdigao J, et al. Clinical performance of a self-etching adhesive at 18 months. *J Dent Res.* 2005;84(Special Issue A): Abstract #1783.
54. Burrow M. Five-year clinical evaluation of One-Up Bond F in NCCL. *J Dent Res.* 2006;85(Special Issue B): Abstract #1153.
55. Sergent R, Burgess JO, Gallo J, et al. In vivo evaluation of two self-etching adhesives, twelve month results. *J Dent Res.* 2006;85(Special Issue A): Abstract #351.
56. Pereira PNR, Swift EJ, Heymann HO, et al. Clinical evaluation of a self-etching adhesive and a flowable composite. *J Dent Res.* 2006; 85(Special Issue A): Abstract #352.
57. Swift EJ Jr, Heymann H, Pereira P, et al. Clinical evaluation of a two-component self-etch adhesive and microhybrid composite. *J Dent Res.* 2006;85(Special Issue A): Abstract #355.
58. Dunn J, Munoz C, Wilson AC, et al. One-year clinical evaluation of Xeno IV in cervical lesions. *J Dent Res*. 2006;85(Special Issue A): Abstract #356.
59. Malmstrom H. 18 months clinical evaluation of a self-etch bonding agent. *J Dent Res.* 2006;85(Special Issue B): Abstract #641.
60. Hanabusa M, Akimoto N, Momi Y. One-year clinical evaluation of one-step self-etching systems. *J Dent Res.* 2006;85(Special Issue B): Abstract #1149.
61. Dalton Bittencourt D, Ezecelevski IG, Reis A, et al. An 18 months' evaluation of self-etch and etch & rinse adhesive in non-carious cervical lesions. *Acta Odontol Scand.* 2005;63:173-178.
62. Dunn JR. iBond. The seventh generation, one-bottle dental bonding agent. *Compend Contin Educ Dent.* 2003;24(2 Suppl):14-18.
63. Tay FR, Pashley DH, Peters MC. Adhesive permeability affects composite coupling to dentin treated with a self-etch adhesive*. Oper Dent.* 2003;28(5):610-621.
64. Hillam R, Pasciuta M, Cobb D. Shear bond strength of primer/adhesives with proprietary dual cure resin cement. *J Dent Res.* 2002; 81(Special Issue A):A-72, Abstract #369.
65. Pasciuta M, Cobb D, Denehy G. Shear bond strength of dual cure primer/adhesives with dual cure resin cements. *J Dent Res*. 2002; 81(Special Issue A):A-76, Abstract #405.
66. Christensen G. Self-etch primer (SEP) adhesives update. *CRA Newsletter.* 2003;27(11/12):1-5.
67. Cheony C, King NM, Pashley DH, et al. Incompatibility of self-etch adhesives with chemical/dual cured composites: two step vs one step systems. *Oper Dent.* 2003;28:747-755.
68. Tay FR, Pashley DH, Yiu CK, et al. Factors contributing to the incompatibility between simplified-step adhesives and chemically cured or dual-cured composites. Part 1. Single step self-etching adhesive. *J Adhes Dent.* 2003;5(1):27-40.