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UNDERSTANDING ADHESIVE DENTISTRY

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ABSTRACT

This review paper firstly provides an outline of the development of resin-based adhesives. A simple classification method is described based on whether an acid etching agent requiring a washing and drying step is used. These systems are called etch and rinse systems. The other adhesives that do not have the washing and drying steps are referred to as self-etching adhesives.

The advantages and disadvantages of these groups of adhesives are discussed. Methods of adhering to the tooth surface are provided, especially where the resin-based adhesive reliability is difficult to control.

INTRODUCTION

The surgical treatment of dental caries and restoration replacement remains a major part of the time to treat patients in any modern dental practice. Philosophically, it has been a long-standing aim for all of us to retain as much tooth structure as possible. Even in the times of GV Black, one of his treatment tenets was to retain tooth structure. In recent times, the introduction of Minimal Intervention or Minimally Invasive Dentistry (MID) has moved the philosophy the next step along to avoid surgical treatment of caries lesions or at least to keep cavity preparations as small as possible.

MID has been achieved due to the development of adhesive restorative materials. The two broad groups of adhesives are the resin-based materials and polyalkenoate acid-based cements. This paper will concentrate on the resin-based materials.

A BRIEF HISTORY

The quest to develop a resin-based adhesive is not new. Buonocore is a name synonymous with the development of the acid-etch technique in 1955 with the classic paper titled '*A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces'*.[1] However, the work of Oskar Haggar predates Buonocore's work when, in 1949, he developed a glycerolphosphoric acid dimethacrylate adhesive, Sevriton Cavity Seal,[†] an adhesive intended for use with Sevriton filling material. This material is, in part, a precursor to the modern day phosphate ester type adhesives. Although not well known, Kramer and McClean identified, using light microscopy, the penetration of this adhesive into the surface of dentine.[2] It could be said this was the first time a hybrid layer was identified and predates Nakabayashi's landmark paper of 1982[3] by 30 years. However, the first attempts at bonding to dentine were not successful. It took another 20 or so years before researchers again revisited the idea of attempting to bond to dentine using resin-based materials. During this period however, the acid-etch technique for bonding to enamel became well established for anterior tooth-coloured restorations.

The next step forward in resin-based restorations was the introduction of Bis-glycidyl dimethacrylate (Bis-GMA) by Bowen in 1962, which revolutionized the tooth-coloured restorations. This resin remains one of the common matrix resin components for current resin composite filling materials.

About the same time as Bowen developed Bis-GMA, Masuhara was investigating the use of tri-n-butyl borane (TBB) as a co-catalyst to facilitate bonding to dentine. This system was incorporated into the product marketed as Palakav.[‡] Work continued on researching various materials in an attempt to form a stable bond and one strong enough to hold a restoration in place as well as to counteract forces from polymerization shrinkage.

In 1965, Bowen introduced N-phenyl-glycine and glycidyl methacrylate (NPG-GMA) used in Cervident, but the clinical 'success' was short-lived.[4] It was not until 1979 when Fusayama and his group published the paper *'Non-pressure adhesion of a new adhesive restorative resin'* in the Journal of Dental Research that a new era of adhesive dentistry commenced.[5] This work was criticized due the use of phosphoric acid on the dentine, which was believed at that time to cause damage to the pulp (Fig.1).

At about the same time Nakabayashi published his 1982 paper describing the layer forming a *new* type of dentine that was made up of dentinal collagen and resin from the TBB, 4-methacryloyloxyethyl trimellitic acid anhydride (4-META), polymethylmethacrylate-based adhesive, Super Bond.[||]This became to be known as the *'Hybrid Layer'* and has been the subject of intensive research that continues even now.

At about the same time Nakabayashi published his work in English, 3M introduced the first version of Scotchbond[§] to Australia. Scotchbond was a two-part adhesive mixed then placed on the cavity surface which yhen penetrated the dentine smear layer forming a weak bond after enamel etching. Acid etching of the dentine remained contentious even up to the early 1990s. During this time the explosion of dentine bonding systems began with such systems as

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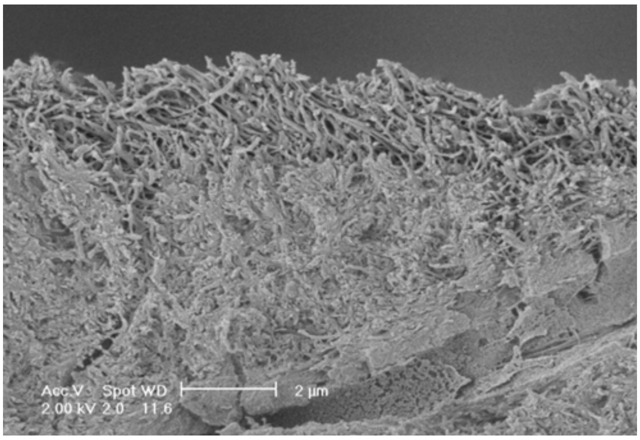

Fig. 1. – Phosphoric acid-etched dentine surface showing the collagen fibre network remaining after the hydroxyapatite has been lost. It is this layer that must be infiltrated by resin to form a good hybrid layer.

GLUMA¶ which used glutaraldehyde and 2- hydroxyethyl methacrylate (HEMA) to bond to dentine in conjunction with the mild etching of EDTA. This system showed some promise clinically. The use of HEMA in adhesive systems from this point became virtually universal due to its ability to bond in a moist environment such as cut dentine due to its hydrophilic nature.

The time of greatest advance in dentine bonding came during the 1990s. Dentine etching methods were changed with the introduction of maleic acid or weaker concentrations of phosphoric acid, the introduction of various priming agents, and later the combination of the priming agents and adhesives. However, the weaker acid etch based systems did not last long due to the etched enamel surface being quite difficult to detect and thus lost popularity with practitioners. At the same time, Kanca described the wet bonding technique, which changed the way bonding was approached, although it failed to simplify the bonding method.[6]

In 1993, the concept of using an acidic resin to etch the enamel and dentine surface was introduced in Japan by the Kuraray Company. This concept has now been widely adopted by manufacturers as an alternative method to the traditional use of phosphoric acid to etch the enamel and dentine simultaneously. This method has now been extended to the point where manufacturers have combined all of the tooth surface treatment steps into one to achieve adhesive to enamel and dentine. Unfortunately, the rapid succession of new adhesives and techniques has led to most practitioners either being confused or unsure of which is the 'best' resin-based adhesive to use clinically.

To answer this question it is necessary to take a step back and analyse what occurs when various adhesives interact with the tooth surface. The concept of generations of adhesives has also served to confuse practitioners even further as there is not a true chronology of the so-called generations of adhesives as they have been developed. The simplest way of classifying resin-based adhesives is to follow the classification proposed by Van Meerbeek's group.[7]

¶ Bayer Dental, Germany

TYPES OF ADHESIVE SYSTEMS

Resin-based adhesive systems can be divided into two broad groups. The first type of adhesive is one that uses an etching agent such as phosphoric acid on the enamel and dentine surface and is rinsed off with an air-water spray. These systems are called '*etch-and-rinse'* systems. The other broad group of systems that do not have a rinse step can be called '*self-etch systems*'. Within these two broad groups the adhesives can further subdivided by the number of steps used to complete the adhesion process.

Etch and rinse systems:

Three-step – these systems use a separate etch, priming agent and resin adhesive. The priming agent is usually a solution of HEMA in a solvent such as water, ethanol or acetone. Its purpose is to make the etched dentine surface more receptive to the application of the hydrophobic bonding resin, which is the third step.

Two-step - these systems have a separate etch and then the priming and bonding steps are combined into a single procedure. These systems require the use of the very technique sensitive 'wet bonding' method. Most of these systems have a volatile solvent of either ethanol or acetone to aid diffusion of the primer-adhesive solution into the etched dentine surface.

Self-etch systems:

Two-step – these systems have an etch and priming step where an acidic resin solubilizes the smear layer and etches the underlying enamel and dentine while it simultaneously primes the tooth surface in readiness for the adhesive. The excess self-etching primer is blown off and with this much of the dissolved smear layer is also blown out of the cavity. The adhesive is then applied and usually air-thinned.

One-step – this group is the newest and simplest of the resin-based adhesive systems. The etch, prime and adhesion steps are combined into a single process. These systems are either two-bottle or one-bottle solutions. The smear layer is again solubilized but remains on the tooth surface. These systems often contain more water than other adhesive systems; this is to help maintain the low pH needed for etching the tooth surface. However, a drawback is the 'all-in-one' adhesives can dissociate more easily as well as incorporating of water into the bond layer.

Each of the two broad groups of resin-based bonding systems have advantages and disadvantages in their use. The etch and rinse systems have been available for the longest period of time and current clinical evidence indicates the three-step etch and rinse systems show reliable long-term results.[8] The disadvantage of these systems is that the stripping of almost all the hydroxyapatite from the dentinal collagen means that complete envelopment of the collagen fibrils is almost impossible and will then create a location for the bond to deteriorate over time. When the hydroxyapatite is completely removed from the dentine surface, the remaining collagen fibre network tends to collapse and shrink after the washing and drying step. With the 3-step systems, the primer, presumably due to its very low viscosity and ability to wet the collagen fibre network is able to infiltrate the

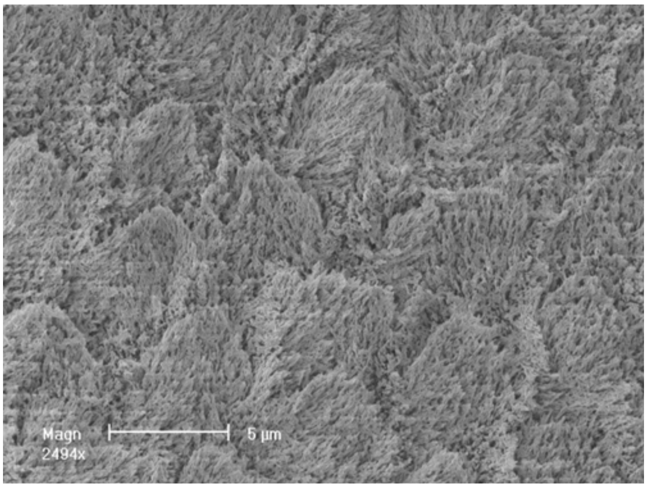

Fig. 2. – Phosphoric acid etched enamel – note the typical etch pattern.

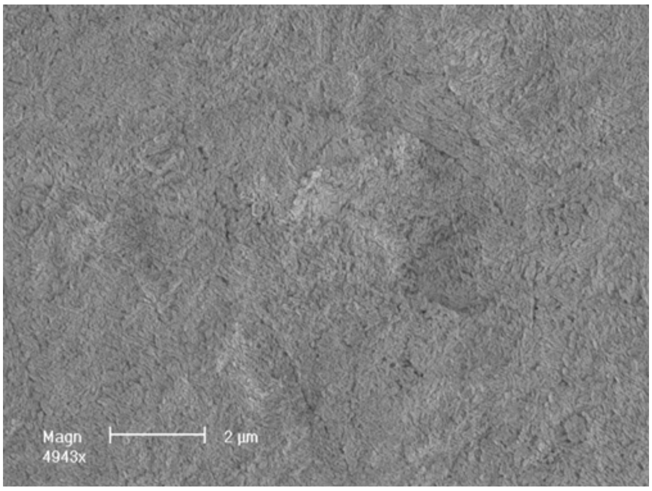

Fig. 3. – Enamel surface etched with SE Primer (Kuraray). The surface of the enamel is not as clearly etched as with the phosphoric acid. However, the surface is roughened, but the current thinking is that a chemical bond is also established with this surface.

collapsed collagen, restore its shape to almost the original form allowing penetration of the adhesive in the third step of the bonding process. This same bonding process is more difficult for the 2-step etch and rinse materials. Hence the need for the 'wet bonding' technique that is achieved by leaving water between the collagen fibrils after the etching, washing and drying steps. The tooth surface has to be left with enough moisture such that collagen fibril shrinkage does not occur. However, the method is extremely difficult to consistently achieve, therefore the technique sensitivity of this bonding method is very high and consistent bonding is difficult to achieve.

The self-etch systems have been shown to be less technique sensitive than the etch and rinse systems.[9] This was shown when novices in bonding were able to achieve outcomes in a laboratory bond test not dissimilar to experienced researchers. However, questions have been raised about the ability of the systems that use a milder pH self-etching solution (around pH 2) to adequately etch enamel that has developed in a fluoridated water supply environment. (Fig. 2 and 3) A comparison of teeth that developed in either a fluoridated or non-fluoridated environment showed that the non-fluoridated tooth enamel did bond more strongly.[10] However, there was no difference in the dentine bond strengths. For the scenario where enamel is either uncut and retains the fluoride rich layer, or enamel is the major source of retention e.g., resin veneer, then phosphoric acid etching of the enamel should eliminate this problem. Clinical evidence is showing that the 2-step self etch systems are performing well and little different from the 3-step etch and rinse systems.[9] The evidence for the 1-step self etch systems is still limited, although promising outcomes are slowly appearing for this group of adhesives.[11,12] A point of note is that some of the new 1-step self etch systems are marketed as a single bottle solutions. These systems seem to dissociate more easily after being applied to the tooth surface. To avoid this, it is essential to follow exactly the application time recommended by the manufacturer and only dispense the adhesive immediately prior to application to the tooth surface to prevent evaporation of the solvent.

The bonding mechanism of most systems, either etch and rinse or self etch systems has been shown to be micro-mechanical with the bond enveloping collagen fibres and hydroxyapatite crystals to form a hybrid layer. However, recent evidence by Yoshida and his co-workers has shown that monomers such as 10-MDP and 4-META are able to form a salt with hydroxyapatite.[13,14] The work has shown, in the case of 10-MDP, that a relatively insoluble salt can be formed with hydroxyapatite. However, in the case of 4-META, the salt is soluble. Nevertheless, this evidence is a clue as to why some of the self etch adhesive systems that contain these monomers show good bond strengths even though the hybrid is much thinner than the etch and rinse systems. These systems are also showing good clinical durability, again supposedly due to the chemical adhesion to tooth structure. The clinical study over 10 years using Clearfil SE Bond** by Akimoto has shown excellent outcomes.[15] It is possible other monomers can also achieve a chemical bond, but evidence of this is still lacking.

When bonding to tooth structure it is not a *'one method fits all'* situation, this is perhaps the greatest misconception by practitioners. The adhesion of different systems, be they etch and rinse or self etch will vary depending on the location of the tooth because the deeper the dentine in the cavity, the greater its surface wetness. The etching process removes smear plugs producing an inherently wetter surface, therefore those systems that do not bond well in a wetter environment should not be used. In this case, systems that do not disrupt the smear plugs are likely to be more reliable on deep dentine. When unsure of the bond reliability of a resin-based adhesive, then a glass ionomer lining is a sound alternative since these materials will adhere to 'wet' dentine.

Bonding to caries-affected dentine is a contentious issue (Fig. 4 and 5). It is known that the caries-affected dentine is less permeable to fluid movement along the dentinal tubules due to occlusion with whitlockite crystals.[16,17] However, caries affected dentine is also inherently wetter and contains slightly less hydroxyapatite. Bonding to this substrate is

**Kuraray, Japan

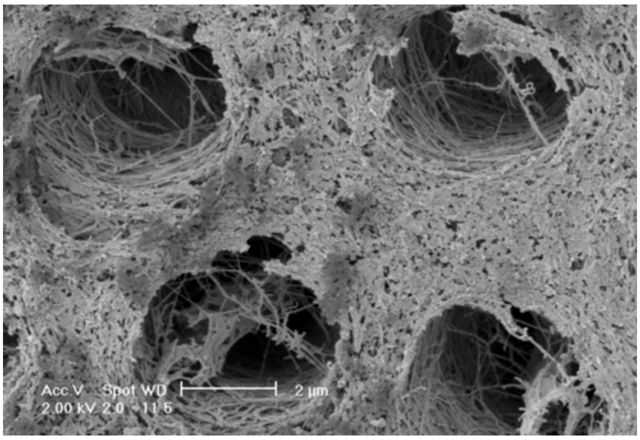

Fig. 4. – 'Normal' dentine surface after etching with phosphoric acid. Note the porosities on the surface that must be infiltrated by resin to form a bond..

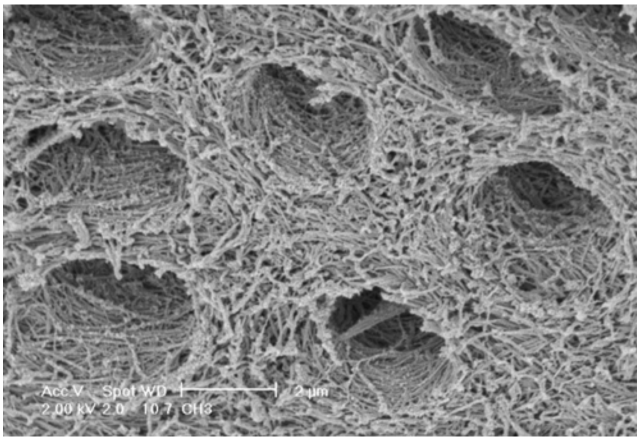

Fig. 5. – Acid etched dentine surface after caries removal with Carisolv® leaving the affected dentine in place. Note the difference in appearance compared with normal dentine. The depth of demineralization is greater and the fibre network more open. This tissue is inherently wetter thus making bonding a little more technique sensitive.

possibly more of a problem for the etch and rinse systems as the etching process tends to remove a greater amount of hydroxyapatite crystals, and to a greater depth, than 'normal' dentine. This therefore makes adhesive resin infiltration more difficult to achieve. The alternatives are either a self etch system or glass ionomer cement.

In the case of restoring a carious proximal cavity, the next question that should be asked in the clinical decision process is where is the proximal margin located? A proximal cavity where the gingival margin of the proximal box approximates the gingival tissues or is as far down as root surface dentine, then bonding of resin based systems becomes much more unpredictable. The most reliable material of choice is a glass ionomer cement using the laminate method (sandwich technique). Ideally a conventional high strength glass ionomer cement should be placed to a thickness of approximately 2 mm along the gingival floor of the proximal box. Once set, the resin-based adhesive can be simply bonded to the GIC surface. The work by Zhang and others has shown that a good bond strength can be achieved with most self etch systems to conventional glass ionomer cements.[18] The bond between the GIC and resin composite was marginally better for the self etch systems compared with the etch and rinse system. It is

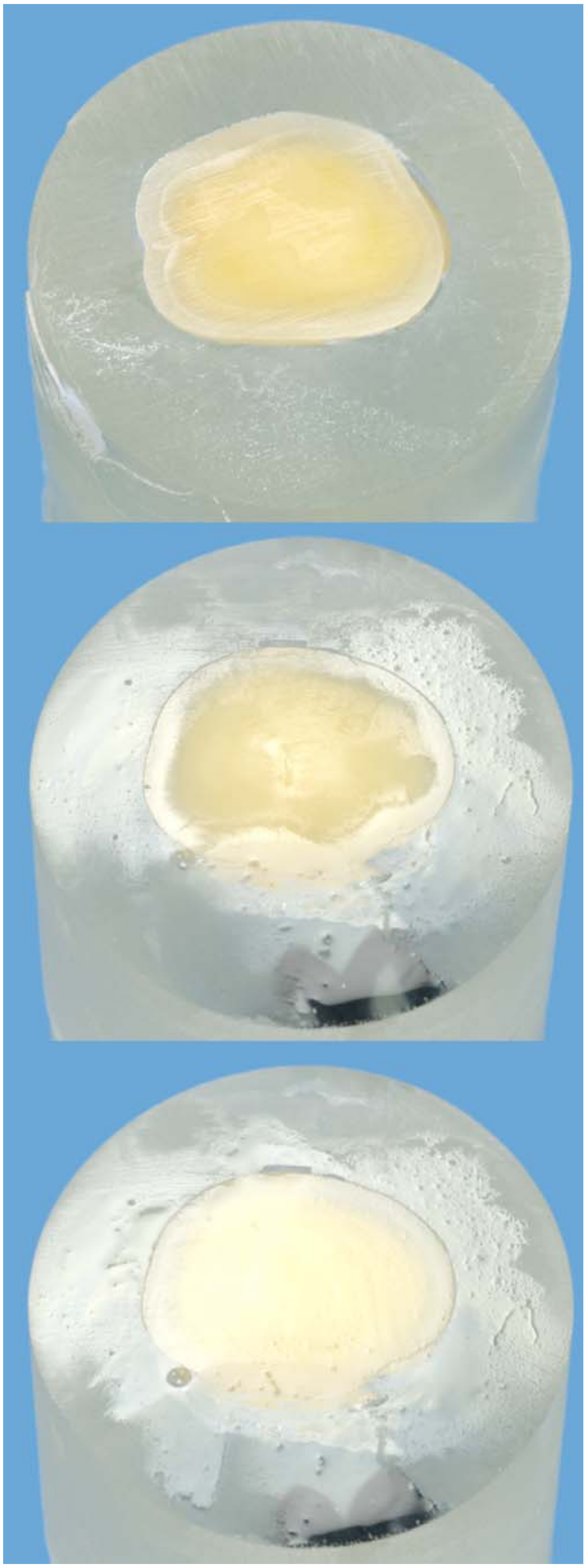

Fig. 6. – Top – prepared enamel and dentine surface. Middle - Enamel/ dentine surface where the self etching primer has not worked correctly on the dentine. Lower – note the patch appearance of the dentine indicating the self-etching primer should be re-applied.

believed the etching, washing and drying steps for the etch and rinse adhesive caused enough crazing of the GIC surface such that it was more likely to fail cohesively compared with the milder etching of the self etch systems tested. Should a GIC-resin laminate method be employed, it is essential to monitor the GIC base. If a patient's oral hygiene is poor in this region there is the potential for dissolution of the GIC,[19] which can be overcome by coating the GIC with either a proprietary coating or with the resin adhesive. Alternatively, a resin-modified glass ionomer cement adhesive could be used to bond to a deep proximal cavity. The only problem here is the potential problems with the light curing of the adhesive.

Finally, one of the difficult aspects of resin adhesion is to know when the adhesive is working properly. Apart from following the application instructions, it is important to look for a change in appearance of the bonded surface. Usually a well bonded surface will have an 'oily/*glossy'* appearance on the dentine (Fig. 6). The only systems where this tends to vary are the single step self etch systems that require very strong air blasting after application. The dentine surface after application of these systems tends to have a matt and occasionally tacky appearance. It is important to use magnification to view the bonded surface. If the surface change is not apparent, then reapplication of the either the self-etching primer in the 2-step or adhesive in the 1-step self etch systems should occur. Similarly for the etch and rinse systems, reapplication of the bond is possible before curing. This should improve the reliability of the bond.

Adhesive dentistry allows us to conserve tooth structure in a way never before possible. This will allow patients to retain teeth for longer. But, adhesive dentistry has brought with it a new level of complexity that means practitioners must consider the benefits and disadvantages of the restoration placement process and be willing to modify techniques as necessary. This is quite different from the almost *'universal'* method that has been used for amalgam when restoring posterior teeth based around the outdated Black's cavity form.

REFERENCES

1. Söderholm K-J, Dental Adhesives…How it all started and later evolved. *J Adhesiv Dent* 2007;9:231-40.

2. Kramer IRH, McLean JW, The response of the human pulp to self-polymerising acrylic. *Br Dent J* 1952;93:150-3.

3. Nakabayashi N, Kojima K, Masuhara E, The promotion of adhesion by the infiltration of monomers into tooth substrates. *J Biomed Mater Res* 1982;16:265-73.

4. Bowen RL. Adhesive bonding of various materials to hard tooth tissues. II. Bonding to dentine promoted by a surface-active co-monomer. *J Dent Res* 1965;44:895-902.

5. Fusayama T, Nakamura M, Kurosaki N, Iwaku M. Non-pressure adhesion of a new adhesive restorative resin. *J Dent Res* 1979;58:1364-70.

6. Kanca J3rd, Resin bonding to wet substrate. 1. Bonding to dentin *Quintessence Int* 1992;23:39-41.

7. Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P et al., Buonocore memorial lecture: adhesion to enamel and dentin: current status and future challeneges, *Oper Dent* 2003;28:215-35.

8. Peumans M, Kanumilli P, De Munck J, Van Landuyt K, Lambrechts P, Van Meerbeek B. Clinical effectiveness of contemporary adhesives: a systematic review of current clinical trials. *Dent Mater* 2005;21:864-81.

9. Sano H, Kanemura N, Burrow MF, Inai N, Yamada T, Tagami J. Effect of operator variability on dentin adhesion: students *vs.* dentists. *Dent Mater J* 1998;17:51-8.

10. Shida K, Kitasako Y, Burrow MF, Tagami J. Micro-shear bond strengths and etching efficacy of a two-step self-etching adhesive system to fluorosed and non-fluorosed enamel. Eur J Oral Sci. 2009;117:182-6.

11. Kubo S, Yokota H, Yokota H, Hayashi Y Two-year clinical evaluation of one-step self-etch systems in non-carious cervical lesions. J Dent. 2009;37:149-55.

12. Van Landuyt KL, Peumans M, Fieuws S, De Munck J, Cardoso MV, Ermis RB, Lambrechts P, Van Meerbeek B. A randomized controlled clinical trial of a HEMA-free all-in-one adhesive in non-carious cervical lesions at 1 year. J Dent. 2008;36:847-55.

13. Yoshida Y, Nakagane K, Fukuda R, Nakayama Y, Okazaki M, Shintani H et al., Comparative study on adhesive performance of functional monomers. J Dent Res 2004;83:454-8.

14. Yoshida Y, Van Meerbeek B, Nakayama Y, Snauwaert J, Hellemans L, Lambrechts P et al. Evidence of chemical bonding at biomaterial-hard tissue interfaces. *J Dent Res* 2000;79:709-14.

15. Akimoto N, Takamizu M, Momoi Y. 10-year clinical evaluation of a self-etching adhesive system. *Oper Dent* 2007;32:3-10.

16. Tagami, J, Hosoda H, Burrow MF, Nakajima M. Effect of Aging and Caries on Dentin Permeability. *Proceedings of the Finnish Dental Society,* 1992;88 (suppl 1):149-54.

17. Banomyong D, Palamara JE, Messer HH, Burrow MF. Fluid flow after resin-composite restoration in extracted carious teeth. *Eur J Oral Sci* 2009;117(3):334-42.

18. Zhang Y, Burrow MF and Palamara J. Bonding glass ionomer cements using resin-based adhesives. *IADR ANZ Division, Pan Pacific Federation Meeting, Wuhan,* China 2009.

19. Scholtanus JD, Huysmans MC. Clinical failure of class-II restorations of a highly viscous glass-ionomer material over a 6-year period: a retrospective study. *J Dent* 2007;35:156-62.

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