New adhesives and bonding techniques. Why and when?

Nicola Scotti, DDS, PhD  
Assistant Professor, Department of Surgical Sciences, Dental School Lingotto,  
University of Turin, Italy

Giovanni Cavalli, MD, DDS  
Private Practice, Brescia, Italy

Massimo Gagliani, MD, DDS  
Associate Professor, Department of Biological Surgical Dental Sciences,  
Giorgio Vogel Dental School, University of Milan, Milan, Italy

Lorenzo Breschi, DDS, PhD  
Full Professor, Department of Department of Biomedical and Neuromotor Sciences,  
DIBINEM, University of Bologna, Alma Mater Studiorum, Bologna, Italy

Correspondence to: Dr Nicola Scotti  
Via Nizza 230, 10100, Turin, Italy; Tel: +39 340 2861799, Fax: +39 011 6620602; Email: nscotti@unito.it
Abstract

Nowadays, adhesive dentistry is a fundamental part of daily clinical work. The evolution of adhesive materials and techniques has been based on the need for simplicity in the step-by-step procedures to obtain long-lasting direct and indirect restorations. For this reason, recently introduced universal multimode adhesives represent a simple option for creating a hybrid layer, with or without the use of phosphoric acid application. However, it is important to understand the limitations of this latest generation of adhesive systems as well as how to use them on coronal and radicular dentin. Based on the findings in the literature, universal multimode adhesives have shown promising results, even if the problem of hybrid layer degradation due to the hydrolytic activity of matrix metalloproteinases (MMPs) still exists. Studies are therefore required to help us understand how to reduce this degradation.

Introduction

It is impossible today to think about restorative dentistry without adhesion. Originally, adhesive systems were mainly provided to perform direct restorations with composite resins; however, the increased need for saving sound tooth structure, coupled with the concept of minimally invasive dentistry, has strongly encouraged the fast evolution of adhesive techniques in recent years.

Since the introduction of the enamel etching concept in 1955,1 bonding technology has focused on the physical, mechanical, and chemical properties in order to improve the clinical longevity of bonded restorations on the one hand, and clinical indications on the other. Today, as adhesive restorations have become the gold standard in esthetic and restorative dentistry, serious efforts have been made to reduce the number of clinical steps needed to obtain good clinical outcomes.

Current adhesives are classified as etch-and-rinse (3- or 2-step), characterized by the use of separate inorganic acids (usually phosphoric acid) to pretreat the dental substrate (Fig 1), and self-etch adhesives containing adhesion-promoting monomers within self-etching primer blends, in conjunction or not with the bonding agent (2- or 1-step) (Fig 2).2

The multistep etch-and-rinse adhesives are often regarded as technique sensitive, with the smallest error in the clinical application procedure resulting in either rapid debonding or early marginal degradation. As a consequence, the demand for simpler, more user-friendly, and less technique-sensitive adhesives remains high. This urges manufacturers to develop new materials that depend less on the skills of the operator for a good clinical outcome.

The most recently developed universal or multimode adhesives are essentially 1-step adhesives, combining acidic priming and bonding in a single solution.3 These adhesives might be indistinctly applied following phosphoric acid pre-etching using etch-and-rinse, selective-etch, or self-etch approaches. Another characteristic of universal adhesives is that they can be used not only on dental substrates (enamel and dentin), but also on composites, glass

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Fig 1  The 3-step etch-and-rinse procedure is highly recommended, with the mandatory step-by-step procedure after rubber dam application. The 0.2% chlorhexidine digluconate application on dentin after phosphoric acid rinse is useful to limit the activity of MMPs and hybrid layer degradation over time.
ceramics, zirconia, and metal alloys.\textsuperscript{5-8} Their versatility in most clinical situations is thus their greatest advantage. However, the fact that clinicians can apply different adhesive protocols (etch-and-rinse, selective etch, or self-etch) to any specific clinical situation may also cause confusion during the clinical adhesive application.

The most recent studies confirm that the gold standard for dentin bonding systems remains the 3-step etch-and-rinse or the 2-step self-etch adhesives.\textsuperscript{9,10} In fact, these systems are characterized by a final step of unsolvated hydrophobic layer that allows adhesive stability over time. It has been proven that adhesive hydrophobicity is crucial in preserving the bond over time, avoiding water penetration of the adhesive layer.\textsuperscript{11} However, it is vital that we simplify clinical procedures in the development of new techniques that are able to provide good clinical results. The aim of the present article is to update the performances of simplified adhesive systems based on findings in the literature, on either coronal or radicular dentin.

Multimode universal adhesive systems

Most of the formulations of recently developed universal adhesives include a chemical bonding capability due to functional monomers to hydroxyapatite, which has been proven to be important for the stabilization of the bond over time.\textsuperscript{10} Among the currently used functional monomers, 10-methacryloxydecyl dihydrogen phosphate (10-MDP) has demonstrated a very effective and durable bonding to dentin. Yoshida et al\textsuperscript{12,13} reported that MDP can ionically bond to calcium (Ca++) ions and form stable MDP-Ca salts, according to the adhesion-decalcification concept. These salt deposits at the adhesive interface form self-assembled nano layers. When the MDP-containing adhesive is applied onto the dentin covered with a smear layer, the surface is partially demineralized up to a nanometer in depth. Ca++ ions released by the partial dissolution of dentin diffuse within the hybrid layer and form MDP-Ca self-assembled nano layers.

\textbf{Fig 2} The 2-step self-etch adhesives show good adhesion on dentin. This method is thus suggested in combination with enamel pre-etching with phosphoric acid in deep cavities, to reduce the risk of postoperative sensitivity and for immediate dentin sealing (IDS) with the build-up before the preparation of the indirect restoration.
In vitro studies have shown that the use of a multimode universal adhesive in either the etch-and-rinse or self-etch application mode did not result in significantly different bond strength to dentin.\textsuperscript{4,14,15} Conversely, due to their higher pH, these adhesives benefit from selective enamel etching.

Based on transmission electron microscopy (TEM) observations, multimode adhesives may be classified as mild or ultra-mild self-etch adhesives when used in the self-etch mode, creating hybrid layers that are approximately 0.5 to 0.2-mm thick. Thus, by blending less acidic resin monomers within the adhesive formulation, the problem of the application mode with 1-step self-etch adhesives appears to be solved. However, a study conducted by Muñoz et al\textsuperscript{5} reported that the application of All-Bond Universal (Bisco Dental) and Peak Universal Adhesive (Optident) in the self-etch mode to dentin resulted in significantly lower microtensile bond strength when compared to the application of those adhesives in the etch-and-rinse mode, while Scotchbond Universal (3M ESPE) was capable of producing similar bond strength to dentin independently of the application mode. This may suggest that an adhesive-dependent technique should be applied in relation to the clinical situation (Fig 3).

A better understanding of the clinical effectiveness of multimode adhesives could be obtained by prospective randomized clinical trials, but as these adhesives have been so recently introduced to the market, there is a lack of medium/long-term \textit{in vivo} studies. An 18-month clinical study by Perdigão et al\textsuperscript{16} showed that retention of class V resin composite bonded with Scotchbond Universal was not affected by the bonding strategy, even if these results could not be considered clinically relevant because of the short follow-up period reported.

**Adhesion to radicular dentin**

The use of adhesive approaches has been expanded to endodontically treated teeth, resulting in several advantages such as avoiding metallic posts and saving as much sound tooth structure as possible. These advantages are directly linked to the reduction of radicular and...
coronal fracture risk, respectively. However, adhesion to radicular dentin could be slightly different, depending on the tissue composition and the portion of the root canal involved.

It has been suggested that endodontically treated teeth are more brittle and may fracture more easily than vital teeth. This could be due to the slight alteration in tissue composition that occurs after endodontic treatment performance.

Interestingly, a change in water content has been observed. In 1972, Helfer et al. already showed that the calcified tissue of pulpless teeth contains 9% less moisture than the calcified tissue of teeth with vital pulps. The loss of moisture was attributed to a change in free water but not in bonded water. In 1992, Huang et al. affirmed that dehydration per se does not weaken the tooth in terms of compressive and tensile strength, but it affects the stiffness and decreases the flexibility of dentin, thus affecting the young modulus of endodontically treated teeth.

A negative impact on dentin composition and structural integrity is also due to sodium hypochlorite (NaOCl) rinses used during endodontic treatment, which strongly affects the protein content of dentin. It has been shown that a 5.25% solution of NaOCl reduces the flexural strength and elastic modulus of dentin, although the deleterious effects of NaOCl on dentin are concentration- and time-dependent, and are not associated with the demineralization caused by the use of ethylenediaminetetraacetic acid (EDTA) as the final active irrigant. However, all the above-mentioned alterations have more of an impact on the dentin mechanical properties rather than the adhesive performance.

**Fiber post adhesion strategies**

There are several resin materials and various methods for cementing fiber posts into root canals. At present, there is no agreement on the best strategy for luting fiber posts. Reliable adhesion is considered a major problem with all types of posts, particularly glass fiber posts because they are luted adhesively to radicular dentin. Rasimick et al. showed that the most commonly reported cause of failure was debonding, which may occur due to several reasons. Firstly, the root canal space is long and narrow, making it extremely difficult to completely remove moisture. Secondly, light inaccessibility is a serious problem, leading to dislodgement of the crown as well as the post and core. As a result, the suboptimally polymerized bonding layer shows a weaker bond strength. Thirdly, the C-factor (the ratio of the bonded to the unbonded surface areas) varies from 1 to 5 in coronal restorations, while it can be higher than 200 in the three-dimensional (3D) environment of the root canal.

Due to the issue of frequent debonding, several studies have investigated and attempted to improve the retention of fiber posts, including different pretreatments of posts and dentin, or the use of different luting agents. Silanization is considered a reliable method to enhance the adhesion of luting fiber posts as it is a fast chairside procedure. However, it was reported that the use of
a silane coupling agent alone or in combination with sandblasting did not significantly increase the bond strengths when self-adhesive luting agents were used.\textsuperscript{35}

Regarding the choice of adhesive system to be used on the root canal dentin, it has been confirmed (as for the coronal portions of vital teeth) that both the 3-step etch-and-rinse and 2-step self-etch systems are the gold standard.\textsuperscript{36}

The rationale of using current adhesive systems is based on the same principle of dental demineralization and simultaneous infiltration by methacrylate monomers. However, root canal and pulp chamber dentin differs from coronal dentin because it has fewer dentinal tubules\textsuperscript{37} as well as different collagen cross-linking in the various dentinal areas. The potential of possible adhesion also varies with respect to the coronal portions of the tooth, and differs along the different adhesive system mechanisms.

Mazzoni et al\textsuperscript{38} compared fiber posts cemented using conventional dual-cure resin-based cements in combination with etch-and-rinse or self-etch adhesives with the more recently formulated self-adhesive cements. Interestingly, the results of this study showed that no difference in bond strength or interfacial nanoleakage expression was observed among the luting strategies. Another study conducted by Bitter et al\textsuperscript{39} concluded that, despite a more uniform hybrid layer and penetration of dentinal tubules obtained with etch-and-rinse techniques, self-adhesive resin cements promoted higher bond strength to root canal dentin. These results support the use of self-adhesive materials, since they are the most simplified and least technique-sensitive materials. The use of self-adhesive cements was also supported in a recent systematic review,\textsuperscript{40} resulting in higher bond strength to dentin due to an effective chemical interaction between the self-adhesive resin cements and root canal hydroxyapatite. The main objective of introducing self-adhesive resin cements was to overcome the drawbacks of other types of cements used to cement indirect restorations to tooth preparations.\textsuperscript{41} This category of materials requires no acid etching, priming, or bonding, which are claimed to be technique-sensitive steps allowing the formation of secondary reactions between the self-adhesive resin and hydroxyapatite by means of chemical bonds.\textsuperscript{42} This bonding mechanism represents an important characteristic when compared to other resin cements that are micromechanically bonded to the dental tissues.\textsuperscript{43}

A simple conclusion about the choice of cement type could be that if clinicians are searching for a simplified cementation system, probably the self-adhesive cements are best. In fact, the application of adhesive bonding system solutions to root canals requires a long operative time and clinical attention due to laborious phosphoric acid removal, uncontrollable moisture presence, primer and bonding accumulation in this deep cavity, and difficulties in achieving a complete light curing. However, the root canal dentin pretreatment could be crucial to the bond strength with self-adhesive approaches. A recent study\textsuperscript{44} concluded that 0.9% saline solution and 2.5% sodium hypochlorite associated with ultrasonic activation seem to be adequate solutions for root canal cleaning.
before fiber post cementation with self-adhesive resin cement, whereas chelating solutions such as 17% EDTA (name of manufacturer? Authors?) QMix (Dentsply), and SmearClear (Kerr Dental) cause a decrease in bond strength because of their effect on calcium, which is fundamental for chemical interactions.

Multimode universal adhesive systems could also be used on radicular dentin, but little information is available on their bond strength to radicular dentin. A recent study by Oskooe et al. compared universal adhesive systems used in an etch-and-rinse and a self-etch approach, in combination with a self-adhesive or dual-curing resin cement on the push-out bond strength to intraradicular dentin. The results showed no bond strength differences between the two tested cements if applied in conjunction with a universal multimode adhesive, which plays a fundamental role in fiber post retention. Interestingly, the adhesive application mode (etch-and-rinse and self-etch) did not influence the bond strength with the dual-curing cement, while the self-adhesive cement improved its bond strength, in conjunction with a self-etch approach with the universal adhesive system. Unfortunately, there are presently no other studies in the literature regarding the bond strength on fiber posts to radicular dentin using multimode universal adhesives. Their effectiveness therefore still needs to be analyzed and evaluated.

Hybrid layer degradation

Independently of the adhesive system employed (etch-and-rinse, self-etch, or multimode), one major problem is limiting hybrid layer degradation over time. It is well known that the process of dental adhesion relies on the creation of an adequate and compact hybrid layer created by the impregnation of the dentin substrate by blends of resin. Thus, the hybrid layer is a mixture of dentin, hydroxyapatite, resin monomers, and residual solvents, and its stability ultimately depends on the resistance of the individual components to degradation phenomena. In general, the more compact and homogenous the hybrid layer, the better the stability of the bond.

The incorporation of hydrophilic and acidic resin monomers in more simplified adhesives substantially improved the initial bonding of contemporary etch-and-rinse and self-etch adhesives to intrinsically wet dental substrates; however, it raised problems associated with the hydrophilic moieties blended within the formulations, leading to failure.

The exact mechanisms responsible for hybrid layer degradation are not fully elucidated; however, degradation of the hybrid layer could be divided into two major problems: 1) hydrolytic degradation of the adhesive resin, and 2) hydrolytic degradation of the collagen matrix within the hybrid layer.

Occlusal forces, acidic chemical agents, and expansion and contraction stresses caused by temperature changes within the oral cavity affect resin stability. The more hydrophilic the adhesive, the more susceptible it is to this type of degradation.

Additionally, incomplete resin penetration into the demineralized dentin matrix or leaching of suboptimally polymerized
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Resin monomers lead to the formation of water-filled, exposed collagen fibrils that are unprotected from denaturation challenges and can be cleaved by endogenous and exogenous collagenolytic enzymes.46

Different strategies have been proposed to prolong the durability of the resin–dentin bond. Primarily, infiltration should be carefully performed as well as polymerization to increase collagen protection.11 Moreover, inhibition of the abovementioned proteases has been recommended using MMP inhibitors such as chlorhexidine,49 quaternary ammonium methacrylates,50 or benzalkonium chloride.51

A different approach is the use of collagen cross-linkers to strengthen the 3D collagen structure and inactivate dentinal MMPs at the same time.52,53

While several studies, both in vitro and in vivo, have been performed on the use of chlorhexidine, the use of collagen cross-linkers in vivo is still under investigation.

Even in root canal dentin, the degradation of exposed collagen by MMPs and cysteine cathepsins at the adhesive interface has been confirmed.55,56 Good results are shown in the literature for the use of chlorhexidine as post space pretreatment,57-59 confirming its positive effect in bond strength preservation after 1 year of storage. However, as with coronal dentin, alternative techniques with collagen cross-linkers seem to show promising results in radicular hybrid layer preservation over time.60,61

Conclusions

In conclusion, the studies that are currently available report that:

- The gold standard for adhesion to coronal dentin are the 3-step etch-and-rinse and the 2-step self-etch adhesives, even if multimode universal adhesives significantly improved their bonding capabilities, and may represent a valuable alternative with reduced technique-operator sensitivity.

- Adhesion to radicular dentin is still a difficult task, and since no difference has been found between different luting approaches, the use of self-adhesive cements is supported due to their intrinsic simplicity and reduced operator-technique sensitivity.

- Degradation of the adhesive interface is still a major issue in adhesive dentistry; however, the use of chlorhexidine as an additional therapeutic primer can be a simple clinical way to improve bond stability over time.
References


