Have Dentin Adhesives Become Too Hydrophilic?

(Les adhésifs dentinaires sont-ils devenus trop hydrophiles?)

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Sommaire

Cet article passe en revue les tendances actuelles dans le développement des adhésifs dentinaires et examine l'hypothèse voulant que certaines catégories d'adhésifs dentinaires actuellement disponibles seraient peut-être trop hydrophiles. Les fabricants ont modifié la composition des adhésifs dentinaires, en y ajoutant du méthacrylate de 2-hydroxyéthyle et d'autres résines monomères hydrophiles, afin que les adhésifs se lient mieux à la dentine mordancée intrinsèquement humide. Ces adhésifs en 3 étapes donnent de bons résultats, mais leur utilisation exige plus de temps, et ces matériaux sont plus sensibles à la technique utilisée que les adhésifs simplifiés plus nouveaux. Lorsque les apprêts sont mélangés à des adhésifs en 2 étapes, en utilisant des adhésifs monocomposants et des apprêts automordançants, les adhésifs deviennent plus perméables à l'eau; ils absorbent donc plus d'eau que les générations précédentes d'adhésifs. Qui plus est, les plus récents adhésifs automordançants à application unique sont encore plus hydrophiles et donc plus perméables à l'eau provenant de la dentine liée sous-jacente. Or, cette perméabilité peut causer une grande variété de problèmes, en apparence non reliés, y compris une incompatibilité entre les résines composites à polymérisation chimique ou double et les adhésifs simplifiés et la dégradation accélérée des liaisons résine-dentine.

Mots clés MeSH : *dental bonding; dentin-bonding agents/chemistry; permeability*

Cet article a fait l'objet d'une révision par des pairs.

Early generations of dentin adhesives were relatively hydrophobic, and dry dental substrates were required for bonding. The adhesives were placed on smear layers but could not penetrate through them. The resulting bond strengths were very low. When manufacturers reformulated the adhesives by adding 2-hydroxyethyl methacrylate (HEMA), the adhesives were able to wet the dentin and could tolerate more moisture. This moisture tolerance became very important with the introduction of the "total-etch concept" (simultaneous etching of enamel and dentin).[1] With the advent of contemporary self-etching adhesives, greater concentrations of acidic (ionic) resin monomers were incorporated into the adhesives to enable them to etch through the smear layer and demineralize the underlying intact dentin.[2–4] Although the incorporation of hydrophilic and acidic resin monomers has substantially improved the initial bonding of contemporary total-etch and self-etching adhesives to intrinsically wet dental substrates, few manufacturers have recognized the potential problems associated with these increasingly hydrophilic adhesives. These potential problems may be realized as manufacturers endeavour to simplify adhesives in response to clinicians' demand for adhesives with speedier application and greater user-friendliness. In this paper, some of these issues will be discussed, along with the current trend of simplifying dentin bonding in both the total-etch and self-etching techniques.

Technique Sensitivity Associated with Total-Etch Adhesives

When the total-etch technique was first introduced, the dentin adhesives available at the time required that the dentin surface be dried after acid-etching. It is now known that air-drying of acid-etched dentin causes collapse of the collagen fibril matrix and interferes with resin infiltration.[5] Thus, the strength of resin–dentin bonds was only half that of resin–enamel bonds. The discovery that water or water–HEMA primers could double the strength of resin–dentin bonds led Kanca to introduce the “wet bonding” technique.[6] However, this new technique raised questions about “how wet is wet dentin,”[7,8] which have never been completely resolved. The optimal amount of surface wetness necessary for wet bonding varies among marketed total-etch adhesive systems, which are acetone-based, ethanol-based or water-based.[9,10] Also, it is impossible to simultaneously achieve uniform wetness on the axial, pulpal and gingival walls because of differences in hydraulic conductance between superficial and deep dentin[11–13] and the presence of caries-affected or sclerotic dentin in which the dentinal tubules are partially or completely obliterated by whitlockite crystals.[14–16] Thus, it is not uncommon to have over-wet regions and over-dry surfaces in the same preparation, which causes non-uniform resin bonding.

Total-etch adhesives are more sensitive to technique because optimal hybridization and sealing of dentinal tubules with the wet bonding technique may differ with each bonding system.[17] Although most bonded restorations are retained because there is sufficient well-bonded surface area, a common clinical manifestation of inconsistent bonding within a restoration is the patient’s complaint of postoperative sensitivity.[18–20] If it is necessary to choose between over-drying or over-wetting of total-etched deep dentin, the former is to be preferred, as vital deep dentin is intrinsically wet after removal of the smear layer (**Fig. 1**).[21] Because the volatile adhesive solvent evaporates quickly, the continuous transudation of dentinal fluid through open dentinal tubules before polymerization of the adhesive may result in the entrapment of water-filled blisters along the adhesive interface (**Fig. 2**).[22] As the patient masticates, these blisters may create a pumping effect that causes rapid movement of fluid through the tubules, which in turn may trigger the A-delta nerve fibres in the pulpal–dentin complex.[23,24]

Postoperative sensitivity may be reduced by 1 of 4 methods. The first of these is the use of HEMA-containing aqueous dentin desensitizers, since HEMA is miscible with water and may form a soft hydrogel after polymerization.[25] However, when HEMA-containing primers are used as desensitizers without adhesives, they do not polymerize. Their desensitizing action may be the result of precipitation of plasma proteins within dentinal fluid.[26] The second method involves the use of a resin-modified glass-ionomer cement as a dentin replacement in the sandwich technique.[27] A new technique, the use of oxalate desensitizers after acid-etching of dentin,[28] prevents calcium oxalate crystals, which would reduce bond strength, from forming on the surface. Instead, the oxalate crystals are formed only within the tubules below the surface (**Fig. 3**). Finally, self-etching adhesives that do not remove the smear plugs may be used, thus reducing hydraulic conductance through the dentinal tubules.[29–31]

Technique Sensitivity Associated with Self-etching Adhesives

Another approach to decreasing the technique-sensitivity of wet bonding is to return to dry bonding to smear layers, but using much more acidic monomers dissolved in water–HEMA primers. The materials used with this method are known as self-etching primer adhesives. These water-containing adhesives are acidic enough to etch and prime through thick smear layers and into the underlying intact dentin.[32] Those with a pH between 1.9 and 2.4 incorporate the smear layer into the hybrid layer if the primers are not agitated during etching.[33] If the primers are agitated, the smear layer can be dissolved and dispersed into the hybrid layer and the overlying adhesive (**Fig. 4**).[34] All self-etching primers are covered with a more hydrophobic adhesive that seals off the underlying hydrated dentin. Therefore, all self-etching primers involve 2-step adhesive systems.[35]

Although all self-etching adhesives bond reasonably well to ground enamel, there is a general consensus that the milder versions of these adhesives do not etch well on unground, aprismatic enamel (**Fig. 5**), where there is no resin tag formation and little subsurface demineralization for micromechanical retention.[36–38] At a clinical level this may result in staining of the enamel margins, which is occasionally reported.[39] Thus, the creation of bevelled cavosurface margins is helpful for improving the bonding of mild self-etching adhesives to restorations with margins placed in enamel, because this process removes the aprismatic enamel that is resistant to acid-etching.

To make self-etching primer systems even simpler, manufacturers have recently introduced single-step self-etching adhesives, which etch, prime and bond tooth surfaces simultaneously. Some of these all-in-one adhesives have been made more acidic and more hydrophilic than the 2-step self-etching primers.[2,35] One disadvantage of hydrophilic resin systems is that they attract water.[40] It is difficult to evaporate water from these all-in-one adhesives, and, even if evaporation is successful, water will rapidly diffuse back from the bonded dentin into the adhesive resin. This water sorption plasticizes polymers and lowers their mechanical properties.[41] Although hydrophobic dimethacrylates are added to all-in-one adhesives to produce stronger cross-linked polymer networks, the hydrophilic monomers tend to cluster together before polymerization to create hydrophilic domains[42,43] and microscopic water-filled channels called “water trees.”[44,45] These water trees permit movement of water from the underlying dentin, through the hybrid and adhesive layers to the adhesive–composite interfaces.[46]

Incompatibility of Simplified Adhesives with Chemically Cured Composites

It is well known that chemically cured composites that use tertiary amine as a component of the catalyst do not bond well with adhesives containing acidic resin monomers. This is because the acidic monomers in the adhesives deactivate the more basic amines that are used as catalysts for the autopoly-

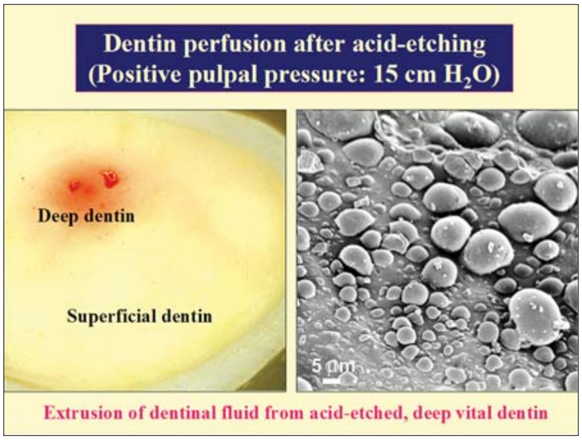

Figure 1: *Scanning electron micrograph of a replica of vital acid-etched dentin shows transudation of dentinal fluid to the surface. Adapted from Itthagarun and Tay.*[21]

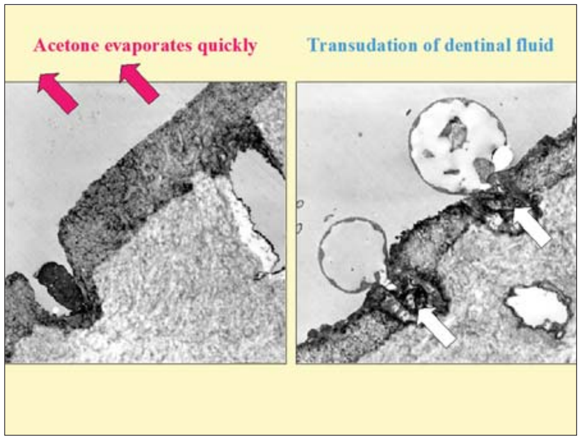

Figure 2: *Dentinal fluid trapped by water-immiscible resins forms water blisters along the resin–dentin interface. Adapted from Pashley and others.*[22]

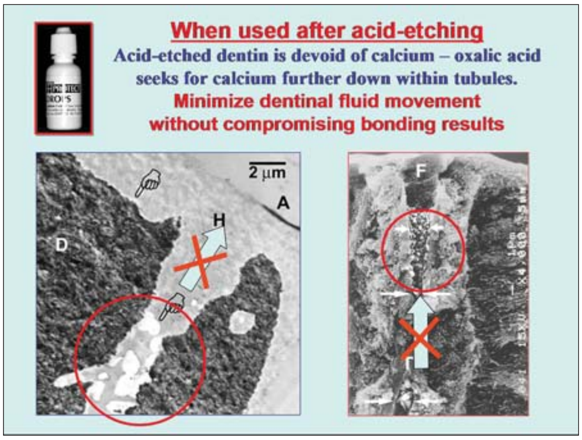

Figure 3: *Scanning and transmission electron micrographs show the result of application of a potassium oxalate desensitizing solution to acid-etched dentin. Calcium oxalate crystals have formed deep inside the dentinal tubules, reducing dentin permeability. Adapted from Pashley and others.*[28]

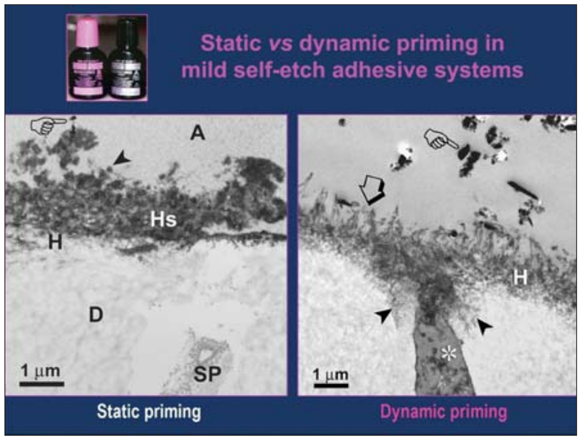

Figure 4: *Transmission electron micrographs show the effect of static and dynamic priming when a mild self-etching adhesive was applied to dentin with thick smear layers. With static priming, a thick hybridized smear layer (Hs) was present, and the underlying hybrid layer (H) was minimal. With dynamic priming, the smear layer was completely dispersed, and a 1-mm thick hybrid layer (H) was created in the intact dentin.*

merization of the composites.[47,48] Clinically, this may result in the debonding of core buildups with self- or dual-cured composites during impression-taking.[49–53] However, this adverse chemical interaction is only partially responsible for the incompatibility between simplified adhesives and chemically cured composites. The other factor responsible for compromising the bonding of chemically cured composites to light-cured adhesives is the recent observation that single-step adhesives behave as permeable membranes after polymerization.[54,55] This apparent incompatibility relates to the fact that both single-bottle total-etch adhesives and single-step self-etching adhesives are used without an additional bonding resin layer.[46,56] In these adhesives, the oxygen-inhibited layer contains acidic monomers that come into direct contact with the chemically cured composite, where they can titrate the basic amine accelerators and inactivate them[57] and also osmotically attract water from the underlying dentin.[58]

The first problem, that of acid–base incompatibility, was reported in 1986[47] but has been largely rectified for many single-bottle adhesives by the introduction of dual-cured versions, which include an additional bottle of chemical co-initiator containing sodium benzene sulphinate.[47,48,58] However, the second problem, that of increased adhesive permeability, has been recognized only recently and occurs only when dentin is used as the bonding substrate. As illustrated with OptiBond Solo Plus (Kerr Corp., Orange, Calif.; **Fig. 6**), the use of a chemical co-initiator improves the tensile bond strength with self- or dual-cured composites to only a certain extent.[56] This problem does not occur when acidic adhesives containing ternary catalytic systems are coupled to enamel or

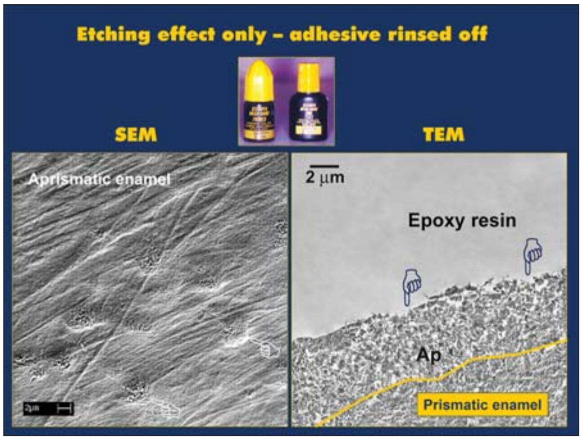

Figure 5: *Scanning and transmission electron micrographs show the effect of a mild self-etching adhesive on uncut, intact enamel. The self-etching primer was rinsed off to demonstrate the etching effect. Adapted from Pashley and Tay.*[36]

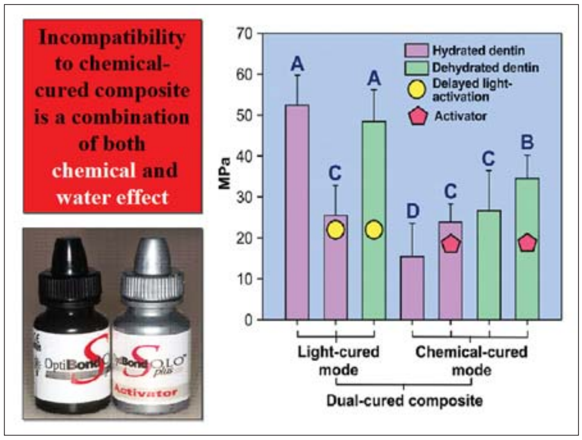

Figure 6: *The incompatibility of single-bottle adhesives with chemically cured composites results from a combination of both chemical (i.e., adverse acid–base reaction) and water (i.e., increase in adhesive permeability) effects; these effects lead to low bond strengths for adhesives containing a dual-cure activator on hydrated dentin. Adapted from Tay and others.*[55]

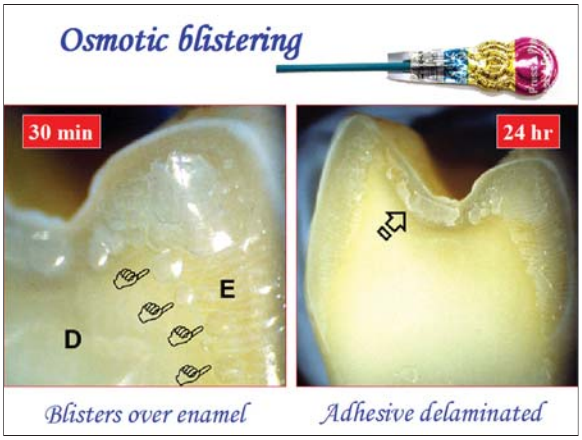

Figure 7: *Demonstration of osmotic blistering when single-step self-etching adhesive was applied to cut enamel and immersed in water. The osmotic blisters, which formed after 10 to 30 minutes, eventually burst, resulting in delamination of the adhesive layer. This delamination does not occur if the adhesives are covered with a more hydrophobic resin layer.*

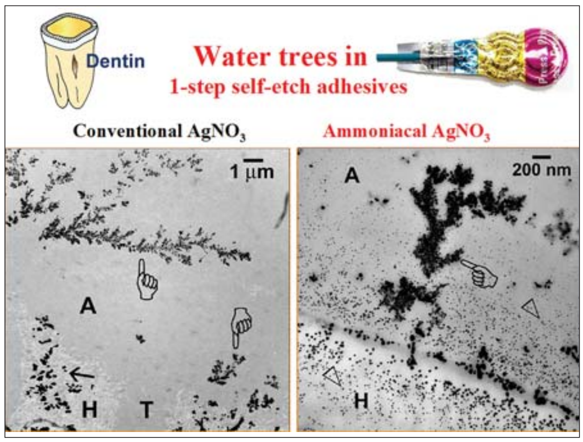

Figure 8: *Water trees (also called water channels) are apparent in transmission electron micrographs of the adhesive layers of some single-step self-etching adhesives after polymerization. These water channels were identified when bonded specimens were immersed in silver nitrate. Adapted from Tay and others.*[43]

processed composites, as these bonding substrates are much less permeable than dentin.[59]

In Vitro Evidence of Adhesive Permeability

To understand just how hydrophilic the simplified adhesives are, any clinician can perform the following experiment. Create a flat tooth surface containing both enamel and dentin. Apply one of the all-in-one adhesives. After curing the adhesive, remove the sticky oxygen-inhibition layer with a moist cotton ball, and immerse the bonded tooth in water. On retrieval after 10 minutes, water blisters will be apparent on the bonded enamel (**Fig. 7**). These blisters are formed by a process commonly known in the resin-coating industry as "osmotic blistering."[60,61] Dissolved calcium and phosphorus ions are probably present within the acidic adhesive as a result of etching of the highly mineralized enamel. These ions osmotically attract water, which diffuses in from the outside through the hydrophilic adhesive layer to create the water blisters. The existence of water-filled channels (water trees) within these adhesives,[60,61] rendering the adhesives permeable, has recently been demonstrated. These water trees were readily observed after the resin–dentin interfaces were immersed in either conventional or ammoniacal silver nitrate (**Fig. 8**). Chemically cured composites polymerize more slowly than light-cured composites, allowing sufficient time for water to diffuse from hydrated dentin across the all-in-one adhesive to form water blisters along the adhesive–composite interface. This phenomenon, demonstrated with an all-in-one adhesive (One-Up Bond F, Tokuyama Corp., Tokyo, Japan) (**Fig. 9**), has been observed with all of the single-step self-etching adhesives.

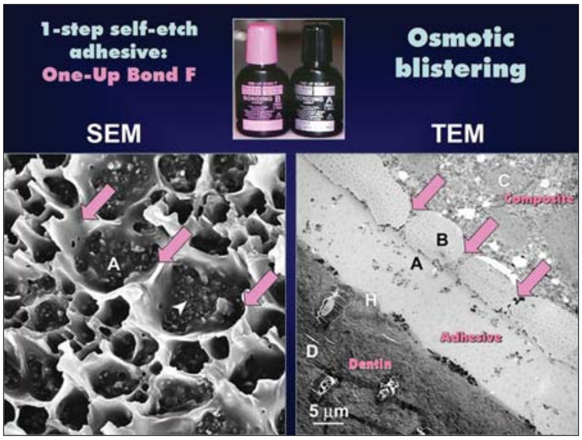

Figure 9: Scanning and transmission electron micrographs of water blisters that formed along the self-cured composite interface with single-step adhesives; these blisters resulted in very weak bonds and premature failure of the adhesive. Adapted from Tay and others.[54]

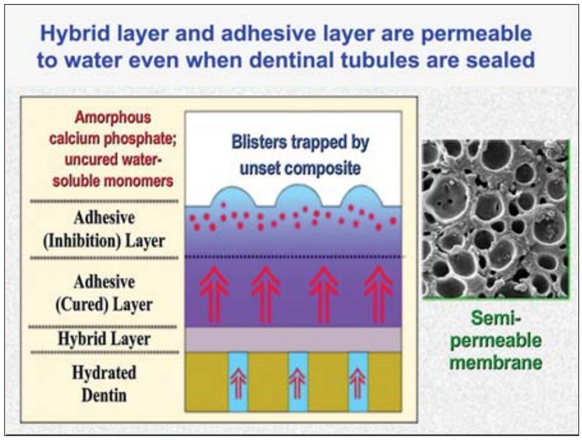

Figure 10: The proposed mechanism of osmotic blistering in dentin adhesives, with the osmotic gradient derived from the oxygen-inhibited layers of adhesives containing a high concentration of ionic monomers and dissolved minerals. Water droplets are trapped by the hydrophobic composite, resulting in a honeycomb appearance when the composite is subsequently polymerized.

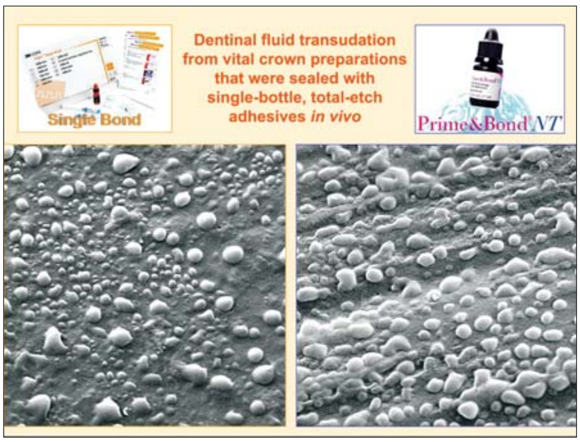

Figure 11: Scanning electron micrographs of epoxy resin replicas of vital crown preparations that were sealed in vivo with single-bottle total-etch adhesives before the impression was taken, as a means of reducing dentin sensitivity. Transudation of dentinal fluid occurred through the polymerized adhesive layers.

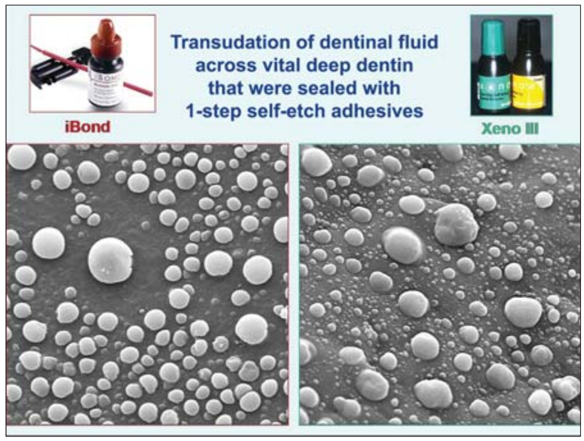

Figure 12: Scanning electron micrographs of similar dentinal fluid transudation along the surfaces of vital crown preparations that were sealed in vivo with single-step, self-etching adhesives. The simplified adhesives did not provide a hermetic seal for vital deep dentin.

It has also been suggested that the osmotic gradient responsible for the induction of this type of water transport is derived from the dissolved ions within the oxygen inhibition layer of these polymerized adhesives (**Fig. 10**).[58]

In Vivo Evidence of Adhesive Permeability

The increase in the permeability of contemporary simplified adhesives (both the single-bottle total-etch adhesives and the single-step self-etching adhesives) to water is readily apparent when they are used for sealing crown preparations of vital deep dentin in vivo before impressions are taken for indirect restorations. In investigations performed by the authors, these adhesives were applied to vital crown preparations, the oxygen-inhibited layer was removed, and impressions of these "sealed" crown preparations were obtained with a low-viscosity polyvinyl siloxane impression material. The impressions were poured up in epoxy resins to produce replicas of the crown preparations for examination with scanning electron microscopy. The results obtained with some of the single-bottle adhesives are shown in **Fig. 11**, and those obtained with single-step self-etching adhesives are shown in **Fig. 12**. The simplified adhesives did not provide a hermetic seal for vital deep dentin (unless they were immediately covered with light-cured resin composites), as evidenced by transudation of dentinal fluid across the polymerized adhesives to form fluid droplets along the surface of the adhesive (**Figs. 11** and **12**). From a clinical perspective, the diffusion of dentinal fluid across the adhesive occurs relatively slowly, so it is unlikely to result in severe postoperative sensitivity. Although water and small ions such as fluoride can certainly move across adhesive-sealed dentin, one wonders if large molecules, such as glucose, bacterial products or hydrolytic enzymes, can permeate from the outside, through the adhesive and dentin, into the pulp. Moreover, the collection of water droplets on the surface of a polymerized adhesive can result in a mode of polymerization of the resin composites that is referred to in polymer chemistry as emulsion polymerization. In such situations, the hydrophobic composite forms an emulsion in the presence of water (i.e., an oil-in-water type emulsion), which results in the appearance of numerous resin beads along the interface instead of a continuous film of polymerized composite. Because resin cements have lower viscosities than resin composites, they are also prone to form resin beads when applied to vital dentin bonded with single-step self-etching adhesives (e.g., ED Primer in Panavia F, Kuraray Medical Inc., Tokyo, Japan).[62] This may cause partial decoupling of bonded indirect restorations and lead to low bond strengths.[63]

Conclusions

The authors of a recent review[64] suggested that technological progress in adhesion between polymeric restorative materials and dentin has been optimized to the point that further major improvements should not be anticipated within the next decade. However, the authors of the current review do not concur with this assessment. The simplification of bonding steps has not improved the quality or the durability of resin–dentin bonds. Although the increased permeability of acidic adhesives to water is probably responsible for their improved fluoride release, water sorption by hydrophilic and ionic resin monomers within both the hybrid layer and the adhesive layer may contribute to the degradation of resin–dentin bond strength over time.[65–69] This phenomenon is aggravated by an increased concentration of hydrophilic resin components in contemporary self-etching adhesives, as the hydrophilicity and hydrolytic stability of resin monomers are generally antagonistic.[70] One solution to this problem is to cover these hydrophilic adhesives with a hydrophobic adhesive (e.g., Scotchbond Multi-Purpose adhesive, 3M-ESPE, St. Paul, Minn.) or a thin layer of flowable composite.[63] Most all-in-one adhesives are simple, easy-to-use self-etching primers that must be covered with a hydrophobic adhesive or composite. This allows the convenience of dry bonding, simplified packaging and simplified bonding procedures without sacrificing bond strength or quality. Admittedly, there have been great advances in knowledge about bonding to dentin during the past decade. More effort should be devoted over the next decade to improving the quality of bonds so as to increase their longevity. ♦

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