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WATER MOVEMENT ACROSS BONDED DENTIN - TOO MUCH OF A GOOD THING

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Over the last decade, the classic concept of 3-step bonding to dental tissues has developed rapidly to more user-friendly, simplified adhesive systems. These comprise the total-etch 2 step, self-etch 2step and the self-etch "all-in-one" adhesives. These adhesives carry along with simplicity some characteristics that are relevant to their efficacy in providing long-lasting bond stability. They share with the glass ionomer cements a class of materials that have high affinity for water. Such hydrophilicity renders such adhesives very permeable and denies their ability to hermetically seal dentin surfaces. Additionally, the water flux across simplified adhesives may compromise bonding in certain circumstances and their durability in the oral environment. This paper presents evidences of the water transport across simplified adhesive systems and glass ionomer cements and relates them with clinical implications of the phenomenon.

UNITERMS: Water-trees; Adhesive systems; Permeable membrane; Resin compatibility; Dentin bonding; Bond degradation.

Bonding of resinous materials to dental hard tissues began in the early 1950s in England by Dr. Oskar Hagger, who developed a monomer based on glycerophosphoric acid dimethacrylate that was chemically-cured with sulphinic acid[1]. His work led to the development of Sevitron, an early commercial adhesive[2]. In the U.S., Dr. Michael Buonocore made the second, and more important advance in adhesive dentistry, by demonstrating that acid-etching of enamel led to improved resin-enamel bonds using Sevitron-like resin formulations[3]. His rationale for acid-etching enamel was that little adhesion was obtained on unetched enamel, which he correctly surmised lacked microscopic porosities for resin infiltration. He knew that concentrated (85 wt%) phosphoric acid was used in industry to pre-treat metal surfaces prior to painting or resin-coating. Thus, it was logical for him to use 85% phosphoric acid for 30 sec to etch enamel, followed by water rinsing. The results of his work were very controversial at the time. Many regarded Dr. Buonocore's approach as unconventional and reckless because he advocated the use of dangerous, industrial-strength acids in the oral cavity.

Adhesive dentistry has advanced significantly since the introduction of enamel bonding almost four decades ago. In a recent Buonocore Memorial Lecture, Van Meerbeek discussed that bonding to dental hard tissues can be effectuated through the use of three different approaches: etch&rinse (i.e. total-etch), self-etch or glass-ionomer approach[4]. The first two approaches involve the use of dentin adhesives to bond to dentin via micromechanical retention. With the glass-ionomer approach, glass-ionomer cements (GICs) and resin-modified glass-ionomer cements (RMGICs) are applied to dentin after conditioning with polyalkenoic acids. Adhesion is achieved via a combination of micromechanical retention as well as chemical adhesion[5]. It is now known that hybrid layer formation is not exclusive to the use of dentin adhesives, as a similar layer develops via demineralization and ion exchange when GICs and RMGICs are applied to enamel (Figure 1) and dentin[6-8].

It is not the intention of this paper to provide an extensive review on bonding of dentin adhesives, RMGICs or GICs to dentin. Rather, evidence of water movement across material-dentin interfaces that are associated with the use of the dentin adhesives, RMGICs and GICs will be illustrated and discussed.

Simplified dentin adhesives

Dentin adhesives are currently available as three-step, two-step and single-step systems depending on how the three cardinal steps of etching, priming and bonding to tooth substrates are accomplished or simplified (Figure 2)[9]. For total-etch adhesives, these three steps are utilized sequentially in three-step systems (e.g. OptiBond FL, Kerr; Scotchbond Multi-Purpose, 3M ESPE). More recently, the three steps have been consolidated into two-steps, of etching and applying two layers of a single-bottle system such as One-Step (Bisco), Prime&Bond NT (Dentsply DeTrey), Single Bond (3M ESPE) and Excite DSC (Vivadent) in which the first layer serves as a primer and the second layer serves as the adhesive[10]. When manufacturers increased the concentration of acidic (ionic) monomers in their primer formulations they created self-etching primer adhesives. Self-etch adhesives eliminate the problem of incomplete resin infiltration within the hybrid layer that is seen when total-etch adhesives are applied to air-dried acid-etched dentin (Figure 3), as etching and bonding is performed simultaneously. Water is an integral component in these adhesives that allows the acidic monomers to be effectively ionized in order for them to demineralize the tooth substrates[11]. These primers combine two steps (etching and priming) into a single step. These primed surfaces are subsequently covered with a more hydrophobic adhesive layer that is light-cured. Examples of such two-step self-etching primers are Clearfil SE Bond (Kuraray), AdheSE (Vivadent) and Tyrian SPE (Bisco). The latest advancement in adhesion technology is the all-in-one adhesives that simultaneously etch, prime and bond following a single application.[11] Examples of these single-step self-etch adhesives include Adper Prompt (3M ESPE), One-Up Bond F (Tokuyama), Xeno III (Dentsply DeTrey) and iBond (Heraeus Kulzer). These adhesives are extremely hydrophilic as they contain high concentrations of both ionic and hydrophilic monomers. Similar to the single-bottle total-etch adhesives, the single-step self-etch adhesives are directly coupled to resin composites without an additional coat of more hydrophobic bonding resin.

There is an ongoing trend to move away from classical multi-component bonding systems toward simplified adhesives that are more user-friendly. The combination of hydrophilic primers and the comparatively hydrophobic bonding resin components in contemporary two-step, total-etch systems and single-step, self-etch systems reflects the clinician-comsumer's desire for operational efficiency and time-saving rather than genuine technological breakthrough. The procedural simplification offered by single-step, self-etching adhesives also reduces technique sensitivity since they are all “dry bonding” rather than “wet bonding” systems. However, simplification should be accomplished without tradeoffs in product quality or bond reliability[12].

Incompatibility with chemical-cured composites

It is known that chemical-cured composites that utilize tertiary amine as a component of the catalyst do not bond well with most single-bottle total-etch adhesives (Figure 4) and all single-step self-etch adhesives (Figure 5). This is because the acidic monomers deactivate the more basic amines[13,14]. Both single-bottle total-etch adhesives and single-step, self-etch adhesives are utilized without an additional bonding resin layer. In these adhesives, the oxygen-inhibited layer contains acidic monomers that come into direct contact with the chemical-cured composite where they can titrate the basic amine accelerators and inactivate them (Figure 6). Clinically, this may result in the debonding of core buildups with self- or dual-cured composites during impression taking (Figure 7)[15-18]. This problem, first reported in 1999, has largely been rectified in many single-bottle adhesives by the introduction of dual-cured versions that include an additional bottle of chemical co-initiator containing sodium benzene sulphinate[14,20]. Examples of these systems include Prime&Bond NT Dual Cure (Dentsply DeTrey), Excite DSC (Vivadent), and OptiBond Solo Plus Dual Cure (Kerr). However, the use of a chemical co-initiator improves its tensile bond strength with self- or dual-cured composites only to a certain extent.[21] A similar situation is observed with single-step, self-etch adhesives. This is illustrated with Xeno CF Bond (Dentsply-Sankin), to which a BondLink (Den-Mat), a generic sodium benzene sulphinate solution was applied before coupling with the dual-cured composites[22]. The two pieces of work described above[21, 22] meticulously showed that adverse chemical interaction is only partially responsible for the incompatibility between simplified-step adhesives and chemical-cured composites. The other factor responsible for debonding of chemical-cured composites from light-cured adhesives is the recent observation that simplified adhesives, the single-step self-etch adhesives in particular, behave as permeable membranes after polymerization[23,24].

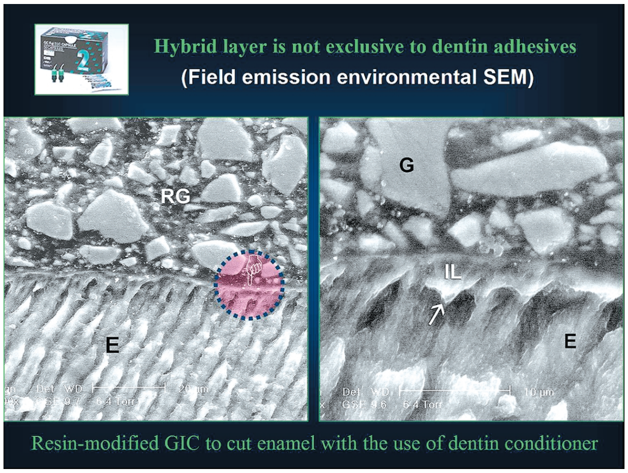


FIGURE 1- Formation of hybrid layers is not exclusive to dentin adhesives. A hybrid layer is formed when Fuji II LC, a resin-modified glass-ionomer cement was applied to cut enamel that was pre-conditioned with polyacrylic acid

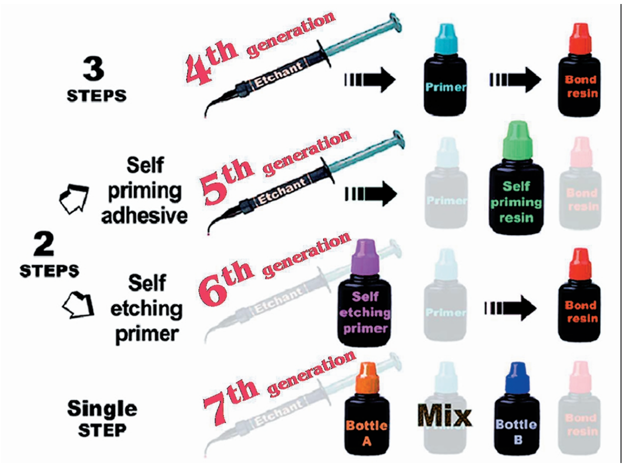


FIGURE 2- Classification of contemporary adhesives into 3-step total etch, 2-step total-etch, 2-step self-etch and the single-step self-etch systems. The 2-step total-etch and the single-step self-etch adhesives may be considered as simplified adhesives in which hydrophilic resins are employed without an additional coating of comparatively more hydrophobic resins

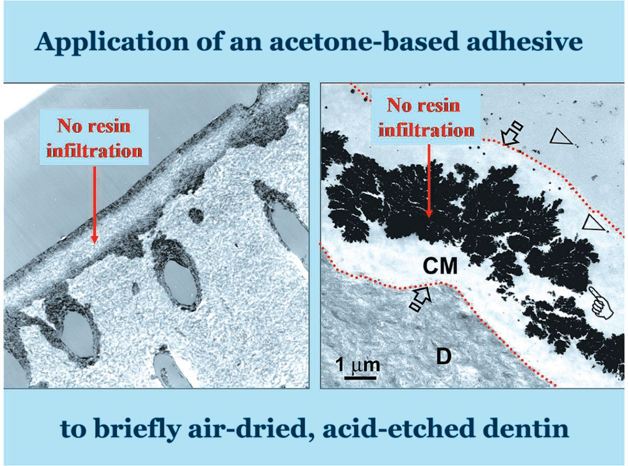


FIGURE 3- Incomplete resin infiltration results when an acetone-based adhesive is applied to briefly air-dried, acid-etched dentin. The regions that are not infiltrated with resin can be seen by the deposition of metallic silver when resin-dentin interfaces are immersed in a silver nitrate tracer solution

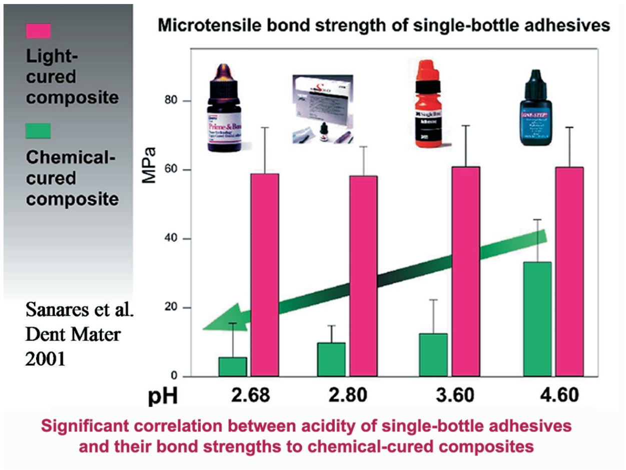


FIGURE 4- Microtensile bond strengths of some common single-bottle, total-etch adhesives decreased significantly when they are coupled to chemical-cured composites. The drop in bond strength is correlated with the acidity of these adhesives

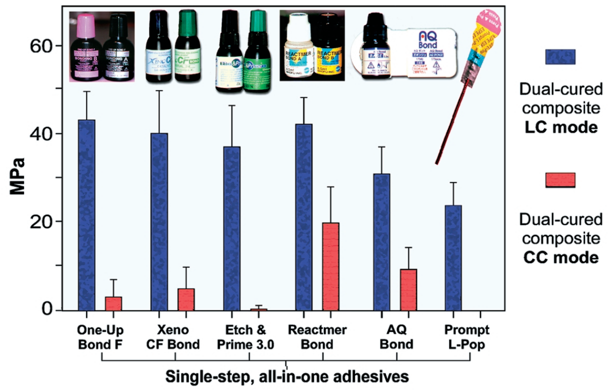


FIGURE 5- A similar effect can be seen in all commercially available single-step self-etch adhesives. Using the same dual-cured composite, microtensile bond strengths decrease substantially in the auto-cured mode when compared with the light-cured mode

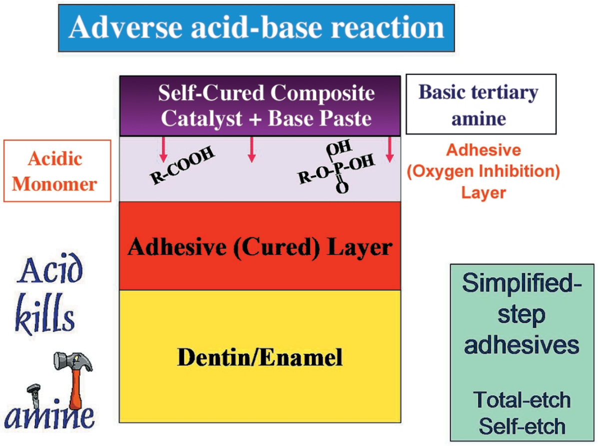


FIGURE 6- Incompatibility between chemical-cured composites and acidic adhesives bonded to dentin is partially caused by the neutralization of the basic tertiary amines in the chemical-cured composite by the residual acidic monomers from the oxygen inhibition layer of the adhesive

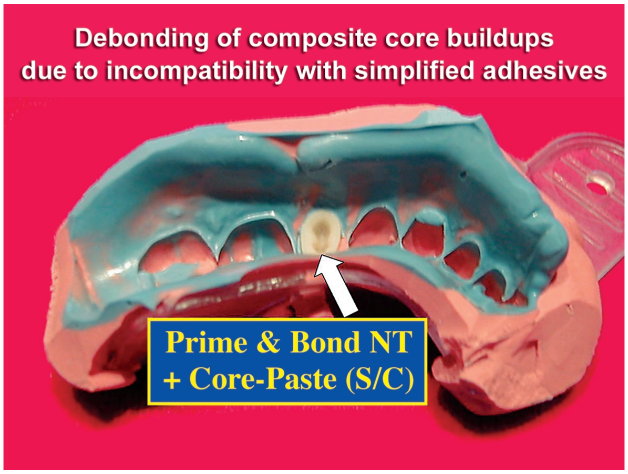


FIGURE 7 - Debonding of composite core buildups can occur when a chemical-cured composite is coupled to an acidic simplified adhesive. The only exception is the single-bottle adhesive One-Step (Bisco, Inc,), that is the least acidic among the simplified adhesives

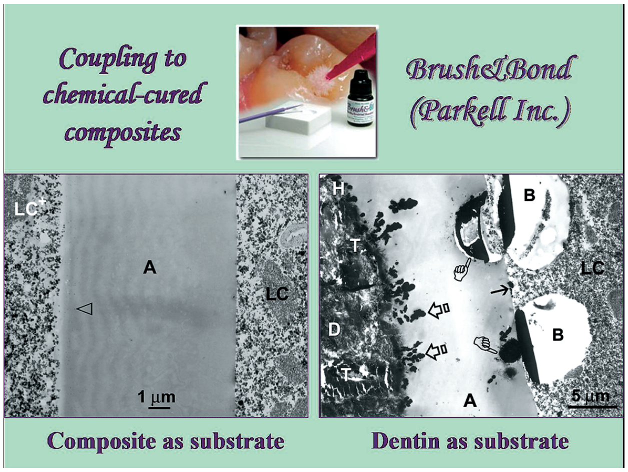


FIGURE 8- Some of the currently available single-step self-etch adhesives (e.g. Brush&Bond, Parkell Inc.) are designed to be bondable to chemical-cured composites. While this works when enamel or processed composites are used as bonding substrates, bonding is poor when dentin is used as a bonding substrate. The permeability of the cured adhesive permits water migration from the underlying dentin to form water blisters along the composite-adhesive interface. These water blisters can act as stress raisers that lower the bond strength of chemical-cured composites to dentin. The black material within the water blisters is metallic silver that were deposited in the blisters after the specimen was immersed in a silver nitrate tracer solution

Simplified adhesives behave as permeable membranes – *in vitro* evidence

It is often surprising to polymer chemists why dentin adhesives containing ternary catalytic systems bond remarkably well to chemical-cured composites, when resin composites, enamel or completely dehydrated dentin were used as bonding substrates[25], and yet poor bonding resulted when normal non-dehydrated dentin was used as a bonding substrate (Figure 8). One simple experiment that can be used to demonstrate that simplified-step adhesives are permeable membranes when bonded to dentin is to place a light-cured adhesive resin on top of moist dentin; then place a light-cured resin composite over the cured adhesive and leave it in the dark for 10-20 minutes before light-activation[23]. Light-cured composites utilize a completely different catalytic system that is generally less sensitive to acidic monomers[26].Thus any adverse reaction observed in light-cured composites cannot be attributed to adverse acid-base reactions. During this period, water will diffuse through the adhesive layer and is trapped in the form of water blisters along the adhesive-composite interface, with the hydrophobic resin composite taking an impression of these transudated water droplets[23]. When these weak interfaces are fractured, the fracture surfaces demonstrate a honeycomb appearance that represents the resin partitions around these water droplets (Figure 9)[24]. Although the phenomenon of water diffusion across a hydrophilic adhesive is novel in dentistry, such a process is commonly known to the resin-coating industry and is termed “osmotic blistering”[27]. It has also been suggested that the osmotic gradient that is responsible for the induction of this type of water transport is derived from the dissolved ions that resided within the oxygen inhibition layer of these polymerized adhesives[24].

Simplified adhesives are permeable membranes and do not provide a hermetic seal of vital deep dentin – *in vivo* evidence

An important goal in conservative dentistry is to restore the peripheral seal of dentin that originally exists prior to the removal of enamel[28]. As the smear layer and smear plugs account for 86% of the total resistance to fluid movement in deep dentin[29], the seal achieved by contemporary total-etch or self-etch adhesives should not be worse than that achieved by the smear layer alone. Conventional thought is that a perfect seal of the resin-dentin interface can be established once the dentinal tubules and spaces within the demineralized collagen matrices are completely infiltrated by adhesive resins. Such a notion is based on the assumption that polymerized resins used for bonding are nonporous and impermeable to fluid movement.

The increase in permeability of contemporary simplified adhesives (i.e. both the single-bottle total-etch adhesives and the single-step self-etch adhesives) to water can be readily seen when they are used for sealing crown preparations of vital deep dentin *in vivo* prior to impression taking for indirect restorations. After crown preparation was performed under local analgesia, we first took impressions of the smear layer-covered dentin using a low viscosity polyvinyl siloxane impression material. Then, we applied these adhesives to the vital crown preparations, removed the oxygen inhibited layer, and took impressions of these “sealed” crown preparations. These impressions were poured up in epoxy resins to produce replicas of the crown preparations for examination using scanning electron microscopy. The result of a single-step self-etch adhesive employed for sealing vital crown preparations, versus the result of the corresponding smear layer-covered dentin are shown in Figure 10. Coalescence of these dentinal fluid droplets can sometimes result in large pools of fluid on the surface of the cured adhesive (Figure 11). For the total-etch adhesives, we went one step further, and took additional impressions of the sealed crown preparations 7-10 days after insertion of the provisional crowns. There was a continuous transudation of dentinal fluid even at the period (Figure 12), with the fluid transudation being more severe for patients who opted for fitting their permanent crowns in the absence of local analgesia (Figure 13). The seal achieved by both the simplified self-etch and total-etch adhesives in areas that were close to the pulp horns were worse than those achieved with the unbonded smear layer.

From a clinical perspective, as the diffusion of dentinal fluid across the adhesives occurs relatively slowly, it is unlikely to result in severe post-operative sensitivity. However, if water and small ions can move across adhesive-sealed dentin, one wonders what the molecular cut-off will be, to prevent the permeation of noxious substances from the outside through the adhesive and dentin into the pulp (Figure 14). In a recent report in which the electrical resistance across total-etch and self-etch adhesive layers was measured before and after bonding, the electrical resistance increased 3-15 fold after bonding compared with the pre-coated smear layer-covered dentin.[30] The electrical resistance was further increased by 5-185 times after the application of a second adhesive coating[30]. In the same study, the authors also pointed out that the increase in electrical resistance was negligible when these conventional adhesives were applied to dentin without the use of the

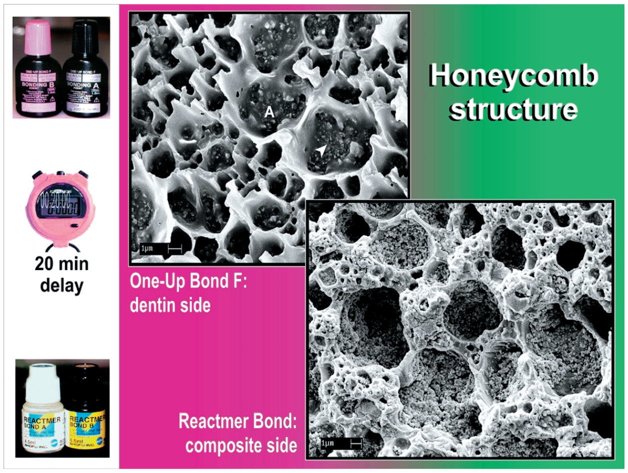


FIGURE 9- When interfaces such as those in Figure 8 are fractured and examined with SEM, the fractured surface revealed the morphology of the fractured water blisters. The water was completely evaporated, leaving behind the resin partitions around the blisters, forming an intricate honeycomb pattern

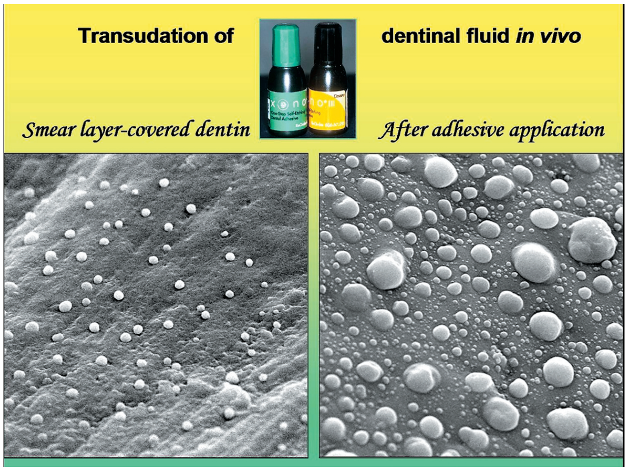


FIGURE 10- SEM micrographs of epoxy resin replicas, comparing the transudation of dentinal fluid from the smear layer-covered dentin and the adhesive-sealed dentin, in a region close to the dental pulp. The crown preparation of the vital tooth was sealed with two coats of a single-step self-etch adhesive, Xeno III. The oxygen inhibition layer was removed prior to impression taking. Transudation of dentinal fluid was sparse in the smear layer-covered dentin, and was more profuse in the adhesive-sealed dentin

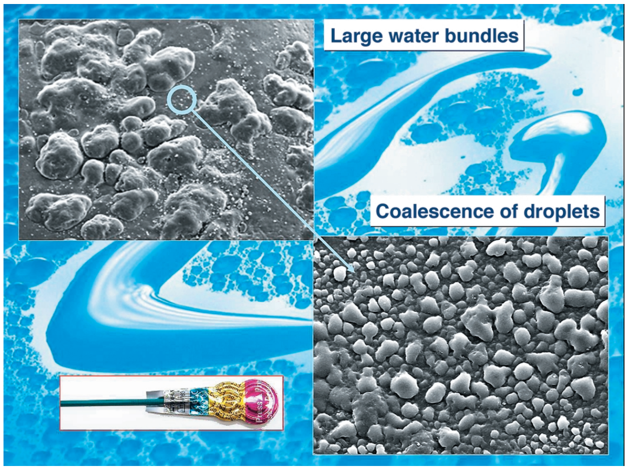


FIGURE 11- SEM micrographs of epoxy resin replicas taken from a vital crown preparation that was sealed similarly with Adper Prompt prior to impression taking. Transudation of dentinal fluid was profuse. Coalescence of individual fluid droplets resulted in the formation of large pools of fluid beneath the impression material

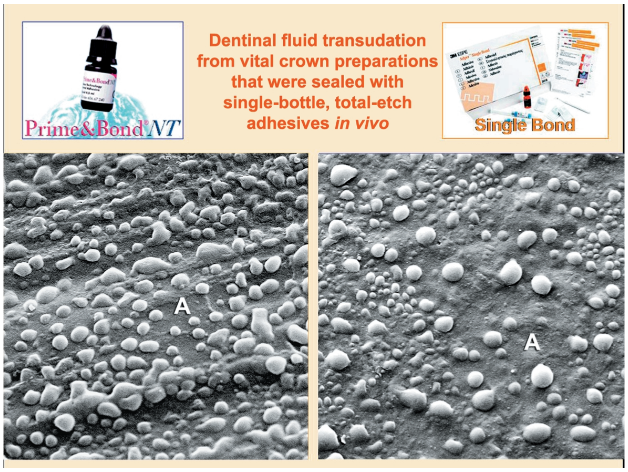


FIGURE 12- Transudation of dentinal fluid from vital crown preparations that were sealed with representative single-bottle total-etch adhesives. The SEM micrographs represented impressions that were taken immediately after bonding and removal of the oxygen inhibition layers

low viscosity bonding resin. These results provided the rationale for the use of the "resin coating technique"[31] when indirect restorations were luted with Panavia F (Kuraray), a resin cement that employs a simplified self-etching primer (ED primer) for bonding to hydrated dentin. In this technique, the dentin is first sealed with a two-step self-etch adhesive (Clearfil SE Bond, Kuraray) and a light-cured, low viscosity microfilled resin prior to impression taking. Indirect restorations were subsequently luted to this resin-coated tooth surface using Panavia F.

Morphologic evidence of adhesive permeability

We have recently demonstrated the existence of two modes of nanoleakage within all single-step self-etch adhesives (Figure 15) and some single-bottle total-etch adhesives (Figure 16) that provide a plausible explanation on the permeation of water through them after polymerization[32,33]. These silver staining patterns can be readily recognized after the resin-dentin interfaces were immersed in ammoniacal silver nitrate. The more easily recognized pattern is in the form of fractal-like, water channels that originate from the surface of the hybrid layer, and extend through the adhesive layer to reach the adhesive-composite interface. These water channels have been given the term "water trees" by Tay and Pashley[34], to reflect their similarities in appearance with those water trees that are formed as a result of water sorption and deterioration of polymer insulation around underground electrical cables (Figure 17)[35]. Water trees, when present, provide the most direct pathways for water movement across the polymerized adhesive layers. Although water trees were initially reported using more technically advanced transmission electron microscopy, they can be similarly observed when silver-stained resin-dentin interfaces are examined using the backscattered mode of a scanning electron microscope. This is illustrated very nicely by the myriad of "unreported" water trees with the resin-dentin interfaces in a recent nanoleakage paper[36]. As chemical-cured composites polymerize more slowly than light-cured composites, this allows sufficient time for water to diffuse from hydrated dentin across the all-in-one adhesive to form water blisters along the adhesive-composite interface.

Although water trees could be seen in all single-step, self-etch adhesives and the ethanol-based single-bottle adhesives, they have not been seen, at least immediately after bonding, in acetone-based single-bottle adhesives[36]. A closer look at the silver staining patterns revealed the presence of a second mode of nanoleakage pattern – the isolated silver grains (Figure 16) – that is universally present in all simplified adhesives. They probably represent hydrophilic domains with the polymerized adhesive that have an increased affinity for water[34-36]. It was initially difficult for us to understand how water movement could occur with the acetone-based, single-bottle adhesives in the absence of direct evidence of water-connecting channels. After studying the literature, we realized that the transport of ions and small molecules across an amorphous polymer matrix may occur in the absence of physically-detectable water channels – via a process known as jump diffusion or ion hopping[37]. This kind of ion hopping mechanism has been commonly observed in polymer ionic conductors, in which ionic salts are incorporated in a polar polymer that possesses significant ionic conductivity[38].

The molecular model depicted above describes the diffusion of penetrant molecules through a polymer matrix in which microcavities of different sizes are formed and destroyed almost continuously (note the atomic time scale in picoseconds)[39] in the polymer. The more hydrophilic the polymer, the greater is the ease of formation of these microcavities, because of the reduced energy required to disruption the adjacent polymer chains. Small, dissolved molecules trapped in these locations are able to move into the direction of a driving force by cooperative motion of adjacent polymer chains. In our two previously described examples, the driving force was derived either from an osmotic gradient within the adhesive that acted as a "hydrophilic solid" in the *in vitro* delayed light-activation experiment, or from a positive pulpal pressure, in the case of the sealing of crown preparations with simplified adhesives *in vivo*.

Water movement across RMGIC-bonded dentin

RMGICs were developed in 1988 by adding polymerizable hydrophilic resins to conventional glass-ionomer formulations[40,41]. These materials were created to overcome some of the problems of moisture sensitivity and low early mechanical strengths associated with conventional GICs, while maintaining their clinical advantages[42]. The basic RMGIC consists of ion-leachable glass, polyalkenoic acid or a modified polyalkenoic acid with a photocurable side chain grafted onto the polymer backbone, a photocurable monomer such as 2-hydroxyethyl methacrylate (HEMA) and water[43]. Unlike conventional GIC, RMGIC has a dual setting reaction. The primary setting reaction consists of free-radical polymerization of the monomeric components. The second setting reaction is the classic acid-base reaction that commences upon mixing of the cement and continues after light-activation. The final set cement contains an interpenetrating network of polyalkenoate salts and a poly(HEMA) matrix[44].

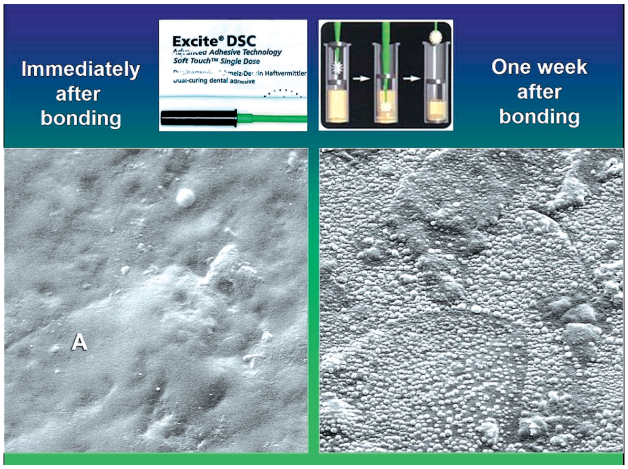


FIGURE 13- Transudation of dentinal fluid continued after the removal of the provisional crown seven days after sealing with another single-bottle adhesive. Fluid transudation was severe in the absence of local analgesia, as there was no vasoconstriction

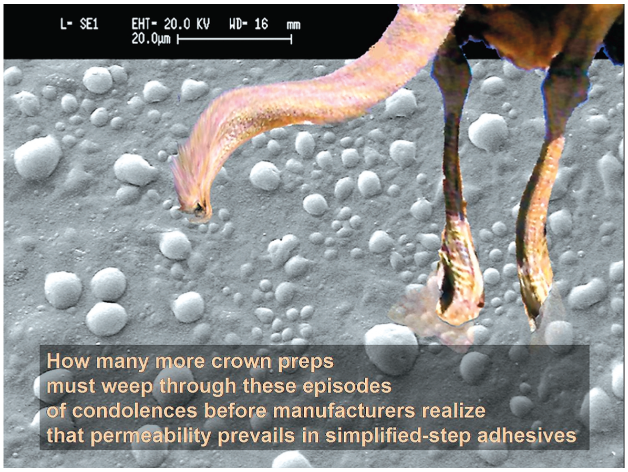


FIGURE 14- Many manufacturers are reluctant to accept that their simplified adhesives are permeable after polymerization. Although dentinal fluid transudation does not occur fast enough with the immediate activation of light-cured composites, the permeability of the adhesives may provide channels for ingress of noxious products, and expediting water sorption that leads to the degradation of resin-dentin bonds

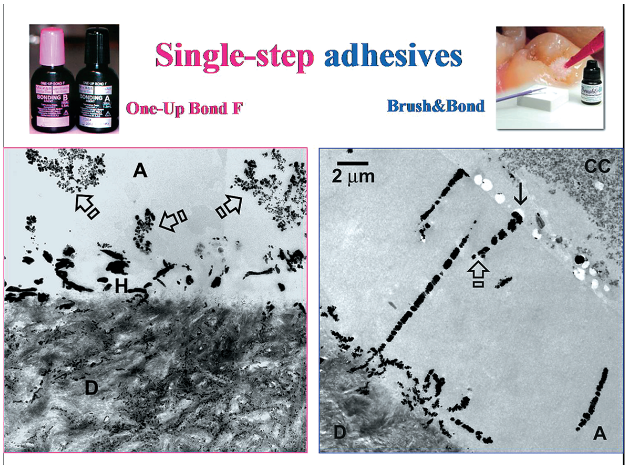


FIGURE15- Water trees that are detected within single-step self-etch adhesives using a silver nitrate tracer solution provide a plausible morphological explanation of the permeability of these adhesives. Direct connection of a water tree with a water blister along the adhesive-composite interface could be seen in the right TEM micrograph

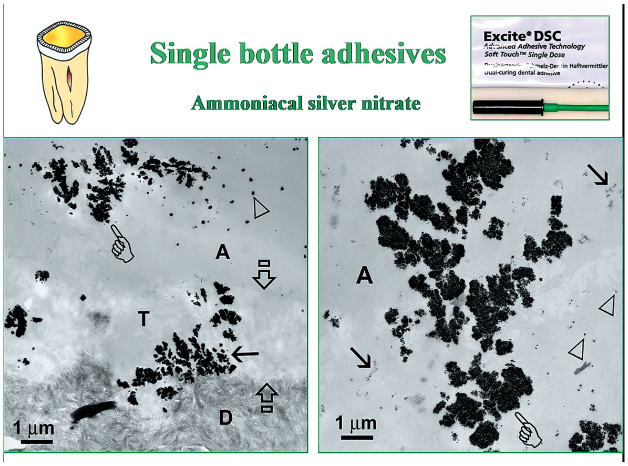
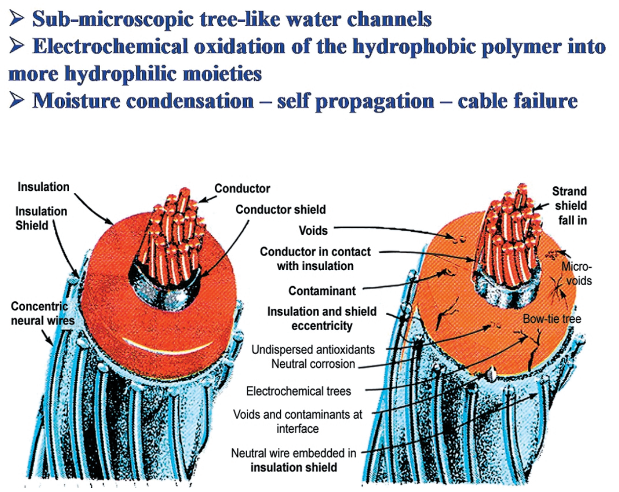
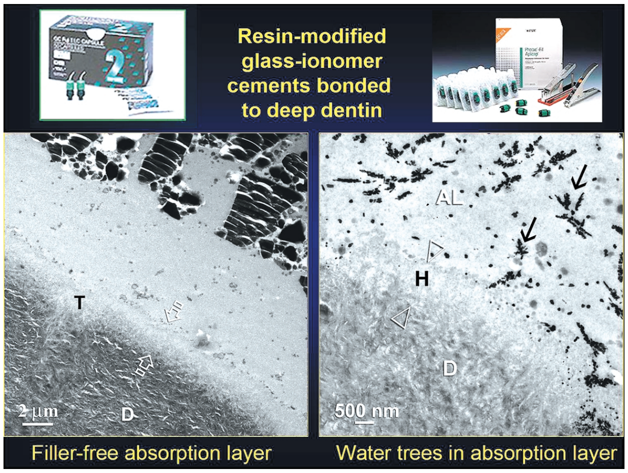


FIGURE 16- TEM micrographs showing the presence of two different modes of nanoleakage within the adhesive layer of an ethanol-based single-bottle adhesive. Water trees are depicted by the pointer, while isolated silver grains, observable only with the use of an ammoniacal silver nitrate tracer, are depicted by the open arrowheads



- ➢ Sub-microscopic tree-like water channels
- ➢ Electrochemical oxidation of the hydrophobic polymer into more hydrophilic moieties
- ➢ Moisture condensation – self propagation – cable failure

FIGURE 17- The term “water tree” was originated from the tree-like deterioration patterns that were found within the polyethylene insulation of underground electrical cables

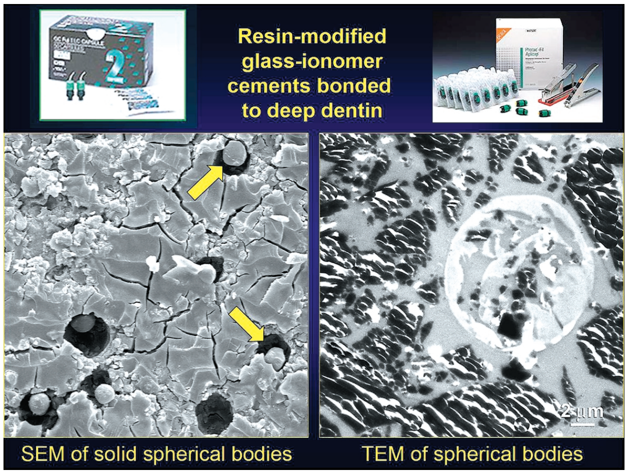


Resin-modified glass-ionomer cements bonded to deep dentin

Filler-free absorption layer

Water trees in absorption layer

FIGURE 18- TEM micrographs showing the presence of a resin-rich, non-particulate absorption layer on top of the hybridized dentin when a resin-modified glass-ionomer cement was applied to deep, polyacrylic acid-conditioned dentin. When these interfaces were immersed in ammoniacal silver nitrate tracer solution, water trees could be seen within the absorption layer

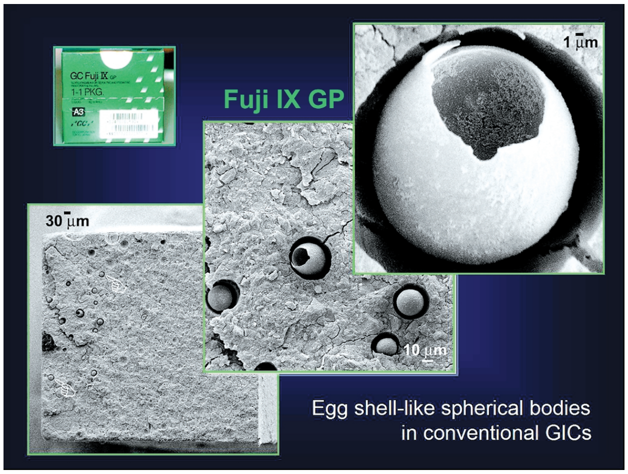


Resin-modified glass-ionomer cements bonded to deep dentin

SEM of solid spherical bodies

TEM of spherical bodies

FIGURE 19- SEM and TEM micrographs showing the presence of solid spherical bodies within the matrices of resin-modified glass-ionomer cements that were fractured close to the bonded moist dentin. These spherical bodies were absent from the air-voids in resin matrices that were fractured further away from the bonded dentin



Egg shell-like spherical bodies in conventional GICs

FIGURE 20- SEM micrographs of Fuji IX, a conventional GIC, that was fractured adjacent to the bonded moist dentin. Egg shell-like spherical bodies could be seen within the air voids that were incorporated in the polyalkenoate matrix

Similar to dentin adhesives, water movement across bonded RMGIC/dentin interfaces were almost completely unknown except for the identification of a 5-15 mm thick, amorphous, non-particulate zone with the use of tandem scanning confocal microscopy when these materials were placed in dentin[45,46]. As this zone was absent when RMGICs were bonded to superficial dentin or enamel, the term "absorption layer" was used to represent its association with water movement within the maturing RMGICs when these materials were placed in deep, moist dentin. The formation of the absorption layer has been attributed to water sorption by the HEMA, or the diffusion of HEMA from the resin matrices of the RMGICs into the water-rich dentin surface probably. The subsequent polymerization of the HEMA resulted in the form of a soft poly(HEMA) hydrogel layer. The RMGIC absorption layer has been thought to act as a stress-breaking layer[47] and may provide a similar function as a dentin adhesive layer in relieving polymerization shrinkage stresses.[48]

The use of the absorption layer as evidence of water movement across RMGIC-bonded dentin has been viewed upon with skepticism because of the limited resolution of the features of this layer, initially reported at an optical microscopical level. The existence of the absorption layer has been confirmed by Tay and Sidhu (unpublished results) using transmission electron microscopy. Such a layer was present in RMGICs that were bonded to moist dentin, but was absent when RMGICs were bonded to completely dehydrated dentin. Using a silver staining technique, water trees could also be identified within the absorption layer and in the resin matrices of RMGICS that were close to the bonded dentin. These water trees provided the channels of water movement for another novel feature that was never reported before in RMGIC/dentin interfaces (Figure 18).

When RMGICs such as Fuji II LC (GC Corp.) and Photac Fil Quick (3M ESPE) bonded to moist dentin were fractured along the cement-dentin interfaces, spherical solid spherical bodies (Figure 19) could be identified with the use of conventional as well as environmental SEM in almost every air void that was close to the bonded dentin, or the absorption layer. Conversely, these spherical bodies were completely absent when fractures were performed at 3 mm away from the cement-dentin interfaces. Using EDX analyses of TEM sections, the internal core of these bodies were devoid of metallic ions. We speculated that the cores of these bodies were made up of a soft poly(HEMA) hydrogel that is similar to the absorption layer along the cement-dentin interface. The periphery of these bodies consisted of a thin crust with fairly high silicon and aluminum content. We believe that these spherical bodies probably represent a continuation of GI reaction and poly(HEMA) hydrogel formation that results from water diffusion from the underlying moist dentin into the air voids that are present within the RMGIC matrix. Their existence provides evidence for the permeation of water through RMGIC/dentin interfaces.

Water movement across GIC-bonded dentin

GICs are regarded as aqueous gels made up of polyalkenoic acid salts around ion-leachable glass fillers and are very hydrophilic after setting. The consequence of water permeation across the GIC-dentin interface is unknown. Using a combination of conventional and environmental SEM, and TEM, we found that absorption layers are not observed in GICs as they do not contain polymerisable resin components. However, similar spherical bodies were seen within the air voids of GICs that were bonded close to the surface of the moist dentin (Figure 20). Unlike those identified from RMGICs, the spherical bodies observed in GICs are eggshell-like (Figure 21) and only consisted of a peripheral silicon-rich phase. These spherical bodies are not artifacts as they could be seen when fractured GICs were examined under wet conditions using field emission-environmental SEM (FE-ESEM) (Figure 22). They were also completely absent in sealed GICs that were fractured at 3 mm away from the bonded dentin (Figure 23). Similar to RMGICs, we believe that the spherical bodies near dentin surfaces result from a continuation of GI reaction, within the air voids of the original polyalkenoate matrix, that occur upon water diffusion from moist dentin.

Water movement across bonded dentin – simplified dentin adhesives vs. GI-based materials

We have seen that water movement across bonded dentin produced dramatically different results in dentin adhesives and in GI-based materials. The advent of dentin adhesives has no doubt improved the quality of preventive, restorative and prosthetic dentistry. However, in the attempt to simplify adhesives by reducing the number of steps, contemporary simplified adhesives are becoming increasingly hydrophilic and tend to be very permeable to water. While there may be no immediate concern when light-cured composites are placed on top of these adhesives and light-cured immediately, the results indicated that simplified adhesives, irrespective of whether they are self-etch or total-etch, do not provide a hermetic seal in the absence of an intermediate layer of more hydrophobic bonding resin[49,50]. These adhesives are even less effective than the original smear layer in

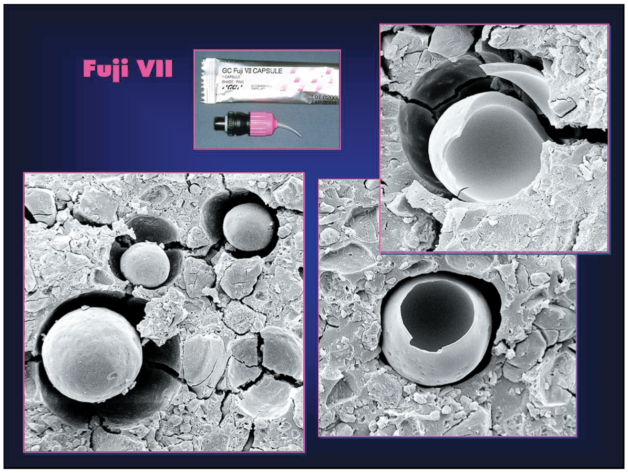


FIGURE 21- SEM micrographs showing similar egg shell-like spherical bodies in Fuji VII, another conventional GIC that contains iron pigment

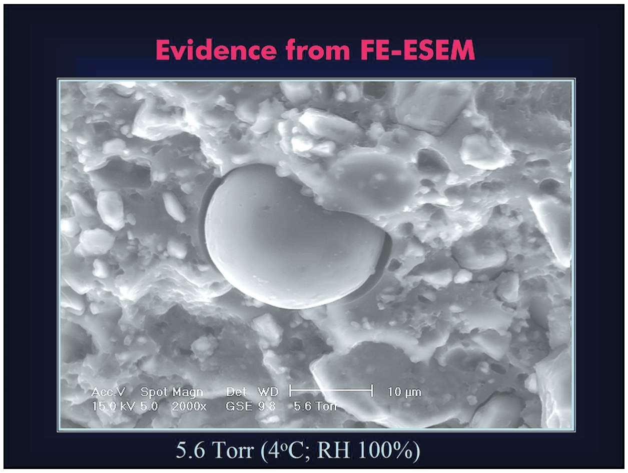


FIGURE 22- Environmental SEM micrograph of an unfractured spherical body in Fuji VII, showing that it is not a dehydration artifact. As the specimen was examined under wet condition, there was no cracking of the polyalkenoate matrix. The spherical body also was well adapted to the air void

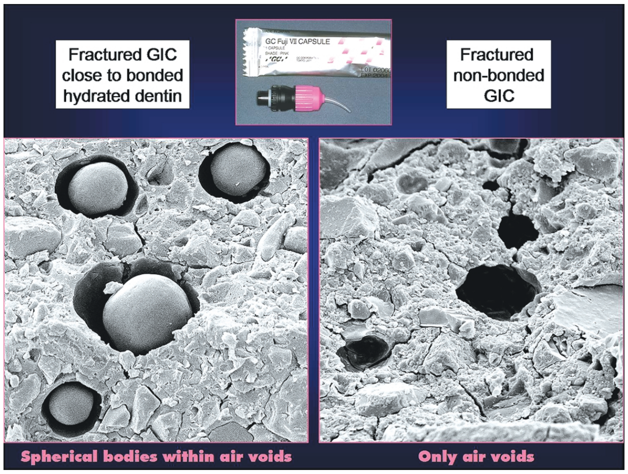


FIGURE 23- SEM micrographs showing the presence of spherical bodies in the matrix of Fuji VII when fractured occurred close to the bonded dentin. Conversely, only air-voids were present when fractured occurred further away from the bonded dentin. The GIC was sealed previously to prevent moist fain or loss from the environment, so that the only source of water available was from the underlying moist dentin

protecting freshly-cut, vital deep dentin, as the use of these solvated adhesives do not coagulate the plasma proteins in the dentinal fluid enough to reduce dentin permeability, as previously shown in an *in vitro* study.[51] Another potentially deleterious issue is that these fluid droplets may contribute to the incompatibility between simplified adhesives and dual/auto-cured composites in direct restorations, and the use of resin cements for luting indirect restorations. The water blisters that are formed may act as stress raisers and form initial flaws that cause subsequent catastrophic failure along the adhesive-composite interfaces in minimally-retentive cavities. It has also been shown recently that both the spaces occupied by the isolated silver grains and water trees will increase in magnitude with the time of storage, and expedite the degradation of resin-dentin bonds[52].

GICs and RMGICs bonded to deep dentin will continue to draw water from the underlying moist dentin for additional acid-base reaction; a process that does not occur with bonded enamel due to its lower water content. The spherical bodies are physical manifestations of the movement of water into pre-existing air voids within these materials. Unlike simplified adhesives in which the transudation of fluid droplets can result in substantial weakening of the adhesive-composite interface, the partial or complete filling up of the air-voids by the spherical bodies may be viewed upon as a self-toughening mechanism of GI-based materials. We hypothesized that these bodies may serve to deflect or blunt any cracks that attempt to propagate through the matrix, thereby toughening the material. The spherical bodies may play an adjunctive role by obliterating porosities in the resin matrix adjacent to the dentin and delay the growth of inherent cracks in this region under loading. The disadvantage is that the GICs and RMGICs may draw water from dentin fast enough to occasionally cause post-operative sensitivity that is associated with their uses. This also provides a rational explanation for the manufacturers' recommendations that GI-based materials be used on slightly moist dentin.

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