

# MAKING SENSE OF DENTIN BONDING AGENTS

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**H**istorical Development Dentin Bonding Agents (DBA) are over a decade old and they are now in to their fourth generation.<sup>1-3</sup> Since their beginning, the understanding of the mechanism of bonding resin to dentin has gone through many changes.

The first generation of DBA (i.e., Cervident, Johnson & Johnson) etched dentin and then applied the NPG-GMA coupling agents developed by Bowen. The hope was to create strong resin tags which bonded to the walls of the dentinal tubules but they proved ineffective. The hydrophobic nature of the adhesive resin prevented penetration into the fluid filled dentinal tubules.<sup>3-6</sup>

The DBA gained widespread popularity amongst clinicians with the introduction of the second generation systems, like Scotchbond (3M) and Universal Bond (Dentsply).<sup>7</sup> These agents used an organo-phosphate ester monomer system that chemically chelated to the calcium component of dentin on the one hand and to polymerized with the composite resin filling material on the other. These agents herald a revolution to restorative dentistry with the expectations that bonded composite resin restorations would soon replace amalgams as the material of choice for direct restorations on posterior teeth. However, these systems also provided minimal bond strength resulting in poor clinical results.<sup>7,8</sup> It was shown through microscopic analysis that these second generation systems failed because they only adhered to the smear layer (SL).<sup>7,9</sup> They were not capable of penetrating through the SL to adhere to the underlying dentin matrix. Pashley showed that bond failure with these systems occurred cohesively between the SL and the underlying dentin and not between the resin adhesive and the SL. Thus the shear bond strengths of these systems were only as good as the bond between the SL and the underlying

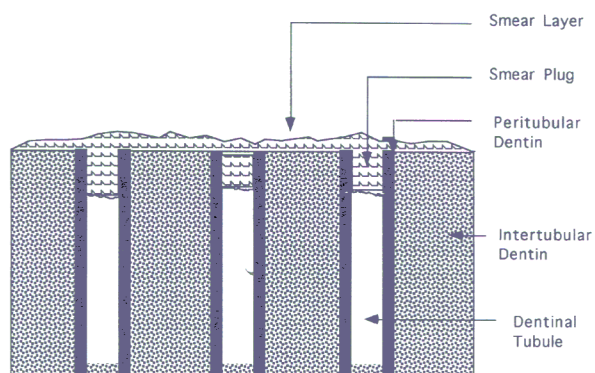
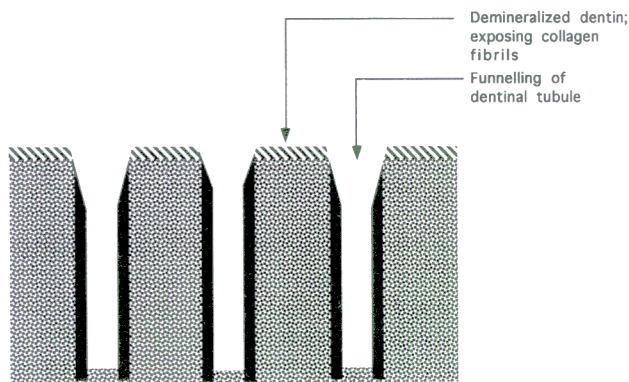


FIGURE 1: INSTRUMENTED DENTIN SURFACE WITH ASSOCIATED SMEAR LAYER.

dentin. This was shown to be around 2-5 MPa, well below the strength believed needed to withstand the polymerization shrinkage stresses of approximately 20 MPa.<sup>7,8,10</sup>

The question then arose as to what to do with the SL. The SL was first described in the early seventies but had little attention during that decade.<sup>11</sup> During the eighties, a renewed interest in DBA development coincided with an increase in the understanding of the SL. The SL is a sheath of debris formed on a tooth surface after instrumentation. In restorative dentistry the high rotational speed of the cutting burr on the dentin surface establishes a wet dusty layer of fragments composed of inorganic constituents with residual denatured collagen and bacteria, which was described in the previous paragraph as being weakly

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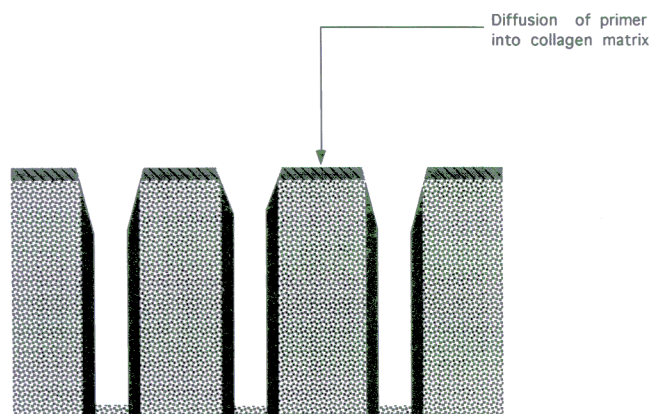


**FIGURE 2:** CONDITIONED DENTIN SURFACE (i.e., ALL-ETCHED) WITH ASSOCIATED EXPOSED INTERDENTAL COLLAGEN FIBRILS AND FUNELLING OF TUBULES.

attached to the underlying dentin.<sup>2,9,12</sup>

Initially it was believed that this layer acted as a natural cavity liner to the exposed dentin surface by plugging the dentinal tubules and thus preventing fluid exchange between the pulp and the outside oral environment. Removing this layer risked opening the tubules and potentially increasing the risk of post-operative sensitivity. The initial sign of failure of the second generation systems was just that; post-operative sensitivity due to penetration of oral fluids through the open gap between the tooth's dentin and the smear layer. Other common clinical signs of clinical failure with this generation of DBA's were marginal discoloration and poor retention.

A newer approach to managing the SL, harnessed in the third generation systems. The introduction of GLUMA (Miles), Tenure (DenMat)



**FIGURE 3:** PRIMED SURFACE.

and Scotchbond2 (3M) worked on the principle of either completely or partially removing the SL and then placing a priming agent to render the surface amenable to bonding.<sup>13</sup> Although the initial bond strengths of these systems were double that of their previous counterparts, they were still half of the goal bond strength of 20 MPa.<sup>1,3,9,13</sup> Therefore, in this case, an improved bond strength did not necessarily translate into a remarkable improvement in clinical success.

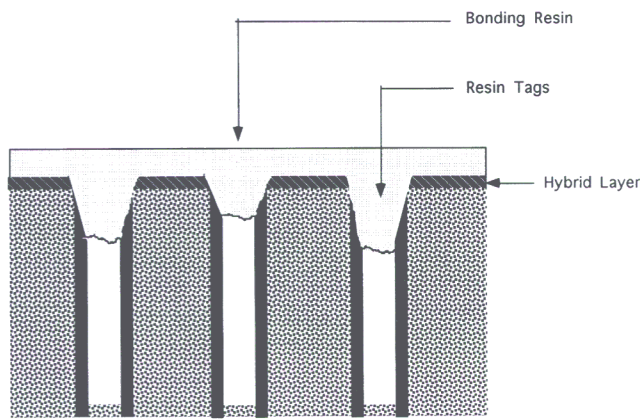
#### FOURTH GENERATION SYSTEMS

Today, the fourth generation DBA systems claim to achieve a bond strength of 20 MPa and even surpasses it.<sup>3,14-16</sup> This system works on the principle of completely removing the SL and demineralizing the superficial layer of dentin. This demineralized dentin layer is about 1-5 m deep.<sup>9,14,17-18</sup> Here, the intertubular collagen matrix is void of hydroxyapatite crystals.<sup>19</sup> Also, the partially dissolved peritubular dentin results in funnelling of the dentinal tubules.

Fourth generation systems ushered in a renewed understanding of the mechanism of dentin bonding. In recent years, there has been significant support for the theory of micromechanical bonding at the adhesive-dentin interface<sup>8,12,14,17,18,20-22</sup> In other words, like enamel, adhesion to dentin is now believed to be micromechanical in nature. Unlike enamel, the predominate bond is not via resin tags in the dentinal tubules. Rather, it is by micromechanical interlocking of the exposed fibrillar collagen in the intertubular dentin with the penetrating adhesive resin. The resultant interfacial structure is referred to as the hybrid layer<sup>24</sup>, resin-impregnated layer<sup>25</sup> or the diffusional layer<sup>26</sup>. In other words, sandwiched between the resin filling material on top and the dentin solid structure on the bottom is a heterogeneous layer of resin and collagen firmly integrated together.

Fourth generation systems are similar to the third generation ones in that their application has multiple steps. The steps are usually divided into the initial conditioning step, followed by the application of a primer and finally a resin adhesive. An acid conditioner (i.e., phosphoric acid, maleic acid, nitric acid) is used to remove from the dentin surface the smear layer and demineralizes the superficial layer of dentin. The primer is a bifunctional monomer that prepares the etched dentin before applying the resin adhesive.<sup>27-29</sup> The nature of this bifunctional chemistry will be discussed later.

These three steps are completed before the placement of the restorative material ( i.e.,



**FIGURE 4:** LAYER OF ADHESIVE BONDING RESIN WITH ASSOCIATED HYBRID LAYER AND RESIN TAGS

composite resins, amalgams, porcelain or resin inlays, onlays and veneers, and metal castings). Some of the fourth generation systems may combine two of the steps into one and be marketed as a two step system. For example, Clearfil Photobond (J. Morita) combines the primer and the resin adhesive into a single application step. While Denthesive 11 (Kulzer) mixes the conditioner and the primer into a single application step.

### THE HYBRID LAYER AND DENTIN BONDING

An understanding of how the hybrid layer is created is essential for the clinician to appreciate what the DBA presently on the market have to offer. As discussed earlier, instrumentation of a dentin surface results in a SL (Figure 1). When this surface is etched (i.e., conditioned), the 1-2 llm of SL is completely dissolved away and 1-5 llm of the dentin surface is demineralized.<sup>9,14,17,18</sup> Funneling of the dentinal tubules occurs and exposure of the

intertubular dentin collagen fibrils are exposed, as depicted in diagram 2. As stated previously, these collagen fibrils are believed to be crucial to the success of the bond generated. If the acid is too harsh or stays on the surface too long, then there is a risk of denaturing the collagen protein resulting in a gelatinous structure, rather than maintaining the desired fibrillar structure. This may have detrimental effects on the final bond.<sup>30</sup> Furthermore, if the concentration of a collagen network is reduced, then inferior bonding is expected.<sup>6,12</sup>

This partially explains why lower bond strengths are found in deep dentin as opposed to superficial dentin. Deep dentin is composed of more tubules and there is less intertubular collagen available for networking. Although deep dentin is rich in peritubular dentin, it is exclusively mineral in composition and therefore plays no part in hybrid layer formation.<sup>31</sup>

The amount of moisture on the prepared dentin surface can also affect bonding. An etched dentin surface has an affinity for water. Therefore, it is impossible to attain an absolutely dry all-etched dentin surface.<sup>32-34</sup> With the newer generations of DBA, a small amount of endogenous dentinal fluid and water, as opposed to saliva or blood, is said to be desirable in order to prevent the collagen fibrils from completely collapsing.<sup>17,18,22,30,35</sup> Prior to etching, the hydroxyapatite crystals stabilize the collagen network in the intertubular dentin. Acid demineralization eliminates this crystalline support. It is the role of the hydrostatic forces of the surrounding moisture to stabilize the collagen into an upright position<sup>17</sup>

The priming agent plays a significant role. When applied to the moist dentin, the primer diffuses into the collagen fibrils, by replacing the surrounding water with a bifunctional monomer. This prevents the collagen matrix from collapsing. These monomers act as the vital link between the adhesive resin above and the dentin surface below. Once it is in place, the curing primer will result in a fixed collagen network wettable enough for the resin adhesive to diffuse into and form the hybrid layer (Figure 3 and 4). The primer is referred to as bifunctional because it has a hydrophilic and hydrophobic component to its chemical structure.<sup>27</sup> The hydrophilic group enables the primer to diffuse into the moist demineralized dentin while the hydrophobic group allows it to polymerize with the overlying resin adhesive.

### BONDING TO MOIST DENTIN

As previously mentioned, the role of moisture of the dentin surface is believed to be essentially for

stabilizing the intertubular collagen fibrils in the standing position. One of the roles of the primer is to exchange itself with the moisture on the dentin surface, while still maintaining the vertical orientation of these fibrils.

The primer is usually mixed with a volatile liquid like acetone or alcohol. These liquids mix with the water on the dentin surface. This mixture decreases the vapor pressure of the dentin surface water. This water evaporates from the surface more readily. This makes it ideal for spreading the monomer over the dentin surface. This is what Kanca describes as the "water chasing" properties of certain primers.<sup>34,36-38</sup>

Although some moisture is believed to favor successful penetration of the primer into the dentin, too much moisture may be deleterious for the establishment of an effective bond between the dentin and the resin.<sup>9,12,33,39-41</sup> Excessive moisture is a problem with deeper dentin surfaces where a greater amount of dentinal fluid bleeding is expected from the abundant number of tubules. This overabundance of water exposure and the reduction of intertubular collagen to network with, are believed to be responsible for the significant drop in bond strengths seen between dentin close to the pulp and dentin near to the dentoenamel junction.

It is debatable how important a role a moist dentin surface prior to applying a DBA plays in a clinical setting. Recently, Vargas et al found that the dry dentin and wet dentin approach to DBA application show equally limited microleakage in an invitro study. Nevertheless, the microleakage of the new generation DBA's were significantly lower than earlier products.<sup>42</sup>

#### THE PHYSIO-CHEMICAL NATURE OF THE CONDITIONER AND THE PRIMER

The ability of the resin adhesive to diffuse into the matrix and form an effective hybrid layer is determined by how well the primer's monomer diffuses and fixes the intertubular collagen fibrils.<sup>43</sup> The quality of this hybrid layer determines the success of the bond between the tooth and the desired restoration. The primer is the determining factor for good bonding to dentin. Conditioning and priming increases the surface energy of the dentin.<sup>32</sup> A wettable surface is created if the surface tension of the primer and adhesive is equal to or less than the surface energy of the etched dentin surface or primed surface respectively. The primer and adhesive must spread and then penetrate 1-5µm deep into the demineralized dentin surface in order

for the eventual establishment of the hybrid layer.<sup>16,23,25,43</sup>

The viscosity of the primer, as well as the resin adhesive, plays an important role on how well they penetrate the surface.<sup>9,32</sup> A less viscous primer is more likely to penetrate more efficiently into the zone. Once diffused, the primer must polymerize in order to lock the collagen fibrils into an upright position. SEM studies have shown that not all DBA systems diffuse equally and probably don't diffuse the full 5µm in depth.<sup>17-20,25</sup> The effect on clinical performance has not been determined. However, what seems to be consistent is that the self-curing (SC) DBA has higher bond strengths than the light-curing (LC) or dual-curing (DC) systems.<sup>9</sup> This is thought to be due to the lower viscosity and complete polymerization seen with the SC systems. LC resin tends to cure towards the light, pulling away from the surface, with less than 60% polymerization, therefore, leaving a softer resin matrix in the hybrid layer susceptible to hydrostatic pressure from the underlying tubular fluid.<sup>2,17,26,27</sup> Further research is needed to determine if the DC systems, with an expected higher amount of polymerization, bond better than LC systems.

#### CONCLUSION

Over the 10 years of DBA development the proposed mechanism of action has gone full circle; from one of mechanical bonding of the first generation DBA to chemical bonding of the second generation, back to micromechanical bonding of the third and fourth generation systems. Presently, the hybrid layer theory appears to be the current model of dentin bonding in vogue. More research is needed to establish the accuracy of this model and its significance to clinical success.

Although there is a large variation in the reported achievements of the many fourth generation DBA's on the market today, they all seem to consistently out perform their predecessor in the laboratory. This we can assume translates into superior clinical performance.<sup>44</sup>

Dentists must make sense of the flood of DBA product available for clinical use. First, a basic understanding of how the hybrid layer is established with the newer DBA systems is essential to appreciate the significance of each application step. Finally, clinicians must carefully follow manufacturer's directions since dentin bonding is a highly technique sensitive procedure.

REFERENCES ARE AVAILABLE ON REQUEST FROM THE MANAGING EDITOR OF ORAL HEALTH.

# SELF STUDY TWO

## QUESTIONNAIRE

1. The original Scotchbond (3M) is an example of a 1st Generation DBA.

- a) True. b)  False

2. Failure of DBA's, such as Universal Bond (Dentsply), was mainly..

- a) cohesively in the composite resin filling material.  
b) adhesively between the composite resin filling material and the bonding in DBA.  
c) cohesively in the DBA resin.  
d) adhesively between the smear layer and DBA.  
e)  adhesively between the smear layer and the underlying dentin.

3. Signs and symptoms of clinical failure of 2nd generation DBA were due to. . .

- a)  post-operative sensitivity due to marginal leakage.  
b) post-operative sensitivity due to polymerization expansion  
c) post-operative sensitivity due to occlusal wear.  
d) a and b  
e) c and d

4. Smear layer formation on the restoratively prepared dentin surface is a resultant of...

- a)  instrumentation with rotational handpieces.  
b) acid etching.  
c) application of DBA.  
d) none of the above.

5. Fourth (4th) generation DBA requires complete removal of the smear layer.

- a)  True. b) False

6. The primary mechanism of adhesion between the DBA and the underlying etch dentin is presently believed to be by...

- a) chemical adhesion  
b)  micro mechanical adhesion between the resin tags

and the dentinal tubules.

- c)  micro mechanical adhesion between the resin and the intertubular collagen matrix.  
d) a and b  
e) a, b and c

7. The resultant interfacial structure between the DBA and the demineralized intertubular dentin is coined as the...

- a) hybrid layer  
b) resin-impregnated layer  
c) diffusional layer  
d)  all of the above.

8. The sequence of application of the 4th Generation DBA's can be described in which of the following order(s)?

- a) conditioning - priming - adhesive resin  
b) acid etching - priming - adhesive resin  
c) priming - conditioning - adhesive resin.  
d)  a and b  
e) a, b and c

9. Hydroxy-ethyl-methyl-acrylate (HEMA) is a common chemical found in the primers of popular DBA's on the market. True or false; HEMA is a bifunctional monomer?

- a)  True. b) False

10 Moisture on the dentin surface before applying the primer is believed to be necessary because...

- a) decicated conditioned dentin surface will cause the collagen matrix to collapse.  
b) a dry dentin surface inhibits the spreading of the primer.  
c) moisture helps maintain the intertubular dentin collagen to be upright.  
d) a and b  
e)  a and c