

On the development of new bonding agents

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Today, there are many different bonding systems on the market so that it is difficult for the dental practitioner to make a proper selection. Generally, the available systems can be divided into two categories, depending on the application technique: self-etch and etch & rinse adhesives. Both kinds of bonding systems rely on the same fundamental mechanism of adhesion to enamel and dentin, which will be explained in the following.



There are two different categories of bonding systems.

Adhesion-Decalcification concept

Dental adhesives primarily bond through micro-mechanical interlocking of the monomers that set within the created surface porosities. Besides micromechanical bonding, certain adhesives con-

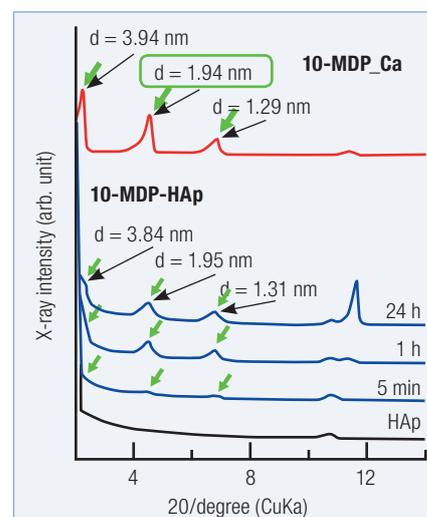
tain functional monomers that have the potential for chemical bonding to calcium in hydroxyapatite when this is remained at the natural dentin structure. This process is regarded as a prerequisite to achieve a stable bond to dentin.

One of the basic models defining the chemical bonding potential is the Adhesion-Decalcification (AD) concept developed by Dr. Yasuhiro Yoshida in 2002. This model explains that a functional monomer either decalcifies or chemically bonds with the tooth structure. The molecules interact with the hydroxyapatite-based substrate, always forming an initial bond with calcium in the first phase. Due to the release of phosphate and hydroxide ions in this phase, the surface remains electro-neutral. In the second phase, there are two different options available. Option 1 is that the bond is not stable and the tooth surface is decalcified, because negatively loaded phosphate ions will attract the positively loaded calcium ions and remove them from the surface. This is basically "etching", like phosphoric acid is well known to do. Option 2 is that the bond remains stable, hydroxyapatite remains available and only limited decalcification occurs, which creates some porosities enabling micro-mechanical interlocking.

Differences of functional monomers / polymers

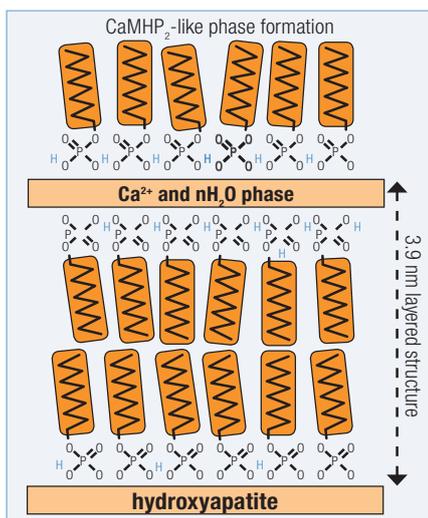
It has been shown that the way of interaction with the tooth substrate is strongly dependent on the functional monomer or polymer. For example, polyalkenoic acid, the functional polymer in glass-ionomers, and 10-methacryloxydecyl dihydrogen phosphate (10-MDP), an acidic functional monomer used in self-etch adhesives, will chemically bond to calcium,

resulting in stable bonds (Option 2). This effect is respectively observed for glass ionomers and 'mild' self-etch adhesive systems that form a small hybrid layer, providing micro-mechanical interlocking as well. Besides the strong chemical affinity to calcium, a specific property of 10-MDP is that it builds a particular nano-sized structure that improves bond stability: the self-assembled so-called 'nano-layering'. This nano-controlled molecular interaction at the interface is detectable by XRD surface analysis or by TEM imaging, and is thought to explain at least in part the well-documented bond durability typically recorded for 10-MDP-based adhesives.



Using XRD surface analysis, nano-layering of 10-MDP becomes visible (peaks).

Other functional monomers used in self-etch adhesives, like 2-methacryloxyethyl phenyl hydrogen phosphate (phenyl-P), and for instance also phosphoric acid will rather decalcify than bond to the dentin surface. This effect is used on purpose in the etch & rinse approach, where the collagen is exposed by use of phosphoric acid (Option 1). In the rinse step, calcium is completely removed from the surface, and a micro-porous network of collagen is exposed up to several micrometers deep. The cre-



Self-assembled nano-layering of 10-MDP.

ated porosities are infiltrated with the adhesive resin afterwards. Using 'strong' self-etch adhesives, the same surface decalcification occurs, but there it raises problems of bond stability since all dissolved but unstable calcium phosphates are embedded in the hybrid layer (and are not rinsed off).

Bond degradation

In the etch & rinse approach, problems like discoloration and secondary decay are often observed at the dentin margins. This should be attributed to phosphoric acid that might be too aggressive on dentin: by a complete demineralization of the dentin surface, the natural protection of collagen by hydroxyapatite is removed; in addition, it is problematic for the resin to penetrate up to the complete depth of decalcification. Therefore, bond degradation is likely to occur over time. So far, several strategies, like 'ethanol wet-bonding' and the use of enzyme (MMP) inhibitors, have been tested to, respectively, improve resin hybridization after an etch & rinse process or to make the bond more resistant against biodegradation.

With the mild self-etch adhesives, separate etching of the enamel surfaces often leads to higher and more stable bond strength than the self-etch technique alone.

The ideal bonding system

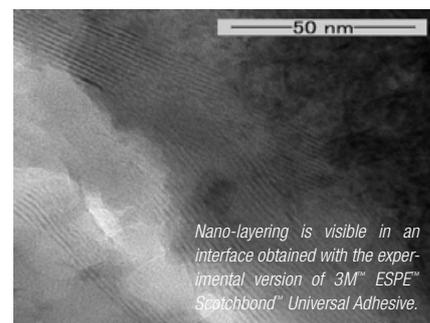
Resulting from all these findings, it can be concluded that today, the most ideal bonding system still involves a three-step-approach: At first, phosphoric acid is applied on the enamel for 'selective' etching. In the second step, a mild self-etch primer with a high chemical bonding potential to hydroxyapatite is used and in step three, a separate solvent-free bonding agent is applied.

A universal adhesive

In view of what general practitioners want, the novel 3M™ ESPE™ Scotchbond™ Universal Adhesive has been developed for both direct and indirect restoration procedures. According to the manufacturer's instructions it can be used optionally in a full etch & rinse procedure, in a full self-etch procedure or in a technique involving 'selective' enamel etching and subsequent self-etching of enamel and dentin. It contains 10-MDP and has a pH value of 2.7. Since it is not too acidic, the hydrolytic stability of the monomers and thus shelf-life of the adhesive is expected to be adequate. In addition, it is composed of dimethacrylate resins, HEMA, the Vitrebond™ Copolymer, filler, ethanol, water and initiators, the latter naturally being of great importance for proper polymerization. Unique is the addition of silane, which is claimed to enable chemical bonding to porcelain following indirect restoration procedures without the need of a separate primer.

Interfaces with Scotchbond Universal

In several in-vitro studies, the interface obtained with Scotchbond Universal adhesive used following the etch & rinse as well as the self-etch approach on bur-cut enamel and dentin was characterised. The results were that 'tight' interfaces were obtained (evaluated TEM images) and that the bond strengths achieved with every technique were in range with those measured for other, often multi-step, 'market-leading' adhesives. Since Scotchbond Universal contains 10-MDP, self-assembled nano-layering was also observed with Scotchbond Universal. For the indirect approach, the bond strength of Scotchbond Universal was tested as well in combination with the novel 3M ESPE ReylIX™ Ultimate Adhesive Resin Cement. The bond strengths to bur-cut enamel and dentin following the self-etch and etch & rinse approaches were in range of those of the controls, even after six months of artificial aging.



Summary

The novel bonding agent showed promising results, even though ageing data and clinical verification are still required. Among the different adhesive modes, the self-etch approach on dentin with separate (selective) enamel etching is strongly recommended with this adhesive as well.