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State of the art of self-etch adhesives

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ABSTRACT

This paper reflects on the state of the art of self-etch adhesives anno 2010. After presenting the general characteristics of self-etch adhesives, the major shortcomings of the most simple-to-use one-step (self-etch) adhesives are addressed. Special attention is devoted to the AD-concept and the benefit of chemical interfacial interaction with regard to bond durability. Finally, issues like the potential interference of surface smear and the more challenging bond to enamel for 'mild' self-etch adhesives are discussed.

1. Introduction

Adhesive technology has evolved rapidly since it was introduced more than fifty years ago. The main challenge for dental adhesives is to provide an equally effective bond to two hard tissues of different nature. Bonding to enamel has been proven to be durable. Bonding to dentin is far more intricate and can apparently only be achieved when more complicated and time-consuming application procedures are followed. Consequently, today's adhesives are often regarded as technique-sensitive with the smallest error in the clinical application procedure being penalized either by rapid debonding or early marginal degradation. As a consequence, the demand for simpler, more user-friendly and less technique-sensitive adhesives remains high, urging manufacturers into developing new adhesives at a rapid pace.

Today's adhesives either follow an 'etch-and-rinse' or a 'self-etch' (or 'etch-and-dry') approach, which differ significantly in the manner they deal with tooth tissue. Nevertheless, it should be stated that both approaches have performed successfully in laboratory as well as clinical research, while obviously there also exists a high product-dependency. Following the previous presentation (and paper) by David Pashley on '*The state of the art of etch-and-rinse adhesives*', the main objective of this presentation (and paper) is to present the latest developments with regard to the self-etch approach.

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2. General characteristics of self-etch adhesives

Different from etch-and-rinse adhesives, self-etch adhesives do not require a separate etching step, as they contain acidic monomers that simultaneously ‘condition’ and ‘prime’ the dental substrate. Consequently, this approach has been claimed to be user-friendlier (shorter application time, less steps) and less technique-sensitive (no wet-bonding, simple drying), thereby resulting in a reliable clinical performance [1–4], though this appeared very product-dependent. Another important clinical benefit of self-etch adhesives is the absence of, or at least lower incidence of post-operative sensitivity experienced by patients (as compared to that associated with etch-and-rinse adhesives) [5–7]. This should to a great extent be attributed to their less aggressive (with respect to dentin and as compared to phosphoric-acid etching) and thus more superficial interaction with dentin, leaving tubules largely obstructed with smear (see below). All these favorable key-features have lead to the steadily growing popularity of self-etch adhesives in today’s dental practices.

Self-etch adhesives can come as ‘two-step’ and ‘one-step’ adhesives, depending on whether a self-etching primer and (mostly solvent-free) adhesive resin are separately provided or are combined into one single solution. One-step adhesives can be further subdivided into ‘two-component’ and ‘single-component’ one-step self-etch adhesives. By separating ‘active’ ingredients (like the functional monomer from water), two-component self-etch adhesives theoretically posses a longer shelf life, but additional and adequate mixing of both components is needed. The single-component one-step adhesives can be considered as the only true ‘one-bottle’ or ‘all-in-one’ adhesives, as they combine ‘conditioning’, ‘priming’ and ‘application of the adhesive resin’, and do not require mixing.

In order to enable (self-)etching, all self-etch adhesives contain water as an ionizing medium. The only exceptions are some commercially available water-free self-etch adhesives. They however require a more technique-sensitive ‘wet-bonding’ application technique (like required for acetone-based etch-and-rinse adhesives) [8]. Sufficient surface-water should then indeed be present to enable self-etching, again leading to the question ‘how wet should dentin be?’ [9]. In general, self-etch adhesives have the advantage to demineralise and infiltrate the tooth surface simultaneously to the same depth, theoretically ensuring complete penetration of the adhesive [10]. With increasing depth, the acidic monomers are gradually buffered by the mineral content of the substrate, loosing their ability to further etch dentin [11,12]. The morphological features of the adhesive-tooth interface produced by self-etch adhesives depend to a great extent on the manner their functional monomers interact with the dental substrate (Fig. 1) [13]. In part depending on the pH of the self-etch solutions, the actual interaction depth of self-etch adhesives at dentin differs from a few hundreds of nanometers following an ‘ultra-mild’ self-etch approach ($pH > 2.5$) (Fig. 1a), which sometimes is being referred to as ‘nano-interaction’ [14], (b) an interaction depth of around 1 μm for a ‘mild’ self-etch approach ($pH \approx 2$) (Fig. 1b), (c) an interaction depth between 1 and 2 μm for an ‘intermediately strong’ self-etch approach (pH between 1 and 2; not shown), and (d) to an interaction of several micrometers deep for a ‘strong’ self-etch approach ($pH \leq 1$) (Fig. 1c). Only with the strong self-etch adhesives typical resin tags are formed at dentin, while they are hardly formed with mild and ultra-mild self-etch adhesives or at maximum the smear plugs get slightly demineralised and subsequently resin-infiltrated.

The actual bonding performance attained by self-etch adhesives varies a great deal, depending not only on the actual class of self-etch adhesives, but certainly also on the actual composition and more specific on the actual functional monomer included in the adhesive formulation (see below).

3. Major shortcomings of one-step adhesives

The latest generation of most simple-to-use one-step adhesives are intricate mixes of hydrophilic and hydrophobic components. These ‘difficult’ mixtures should so far be considered as ‘compromise’ materials that have consequently been documented with several shortcomings (Fig. 2) [15–17]. Generally, a reduced ‘immediate’ bond strength is recorded in comparison to that measured for multi-step adhesives [15,18]. In addition, any kind of ‘aging’ demonstrates a lower long-term bonding effectiveness. Moreover, numerous studies report on increased interfacial nano-leakage [7,19,20]. One-step adhesives that are rich in HEMA, showed enhanced water sorption from the host dentin, in particular when the lining composite is not immediately cured to block these osmosis effects [21,22]. On the other hand, typical is also the phase-separation described for HEMA-free/poor adhesives [23]. An adapted ‘strong’ air-drying procedure provides a means to remove water (that is separated from the more hydrophobic components) from the interfacial area, theoretically enabling better polymerization. While this technique works on relatively flat surfaces, the water ‘bubbles’ (formed once the solvent starts to evaporate, by which the more hydrophobic monomer components no longer remain in solution) are more difficult to blow away in more complex cavity configurations. In addition, mixing all ingredients into one bottle has caused shelf-life problems [24], though recently some manufacturers solved this issue by using more hydrolytically resistant acrylamide monomers [25]. Finally, inferior clinical performance of one-step adhesives confirmed the less favorable laboratory findings, while it must also be said that the latest generation of one-step adhesives definitely perform better [1,26].

4. The ‘AD-concept’ revisited as basis of durable bonding

The fundamental mechanism of bonding to enamel and dentin is essentially based on an exchange process, in which minerals removed from the dental hard tissues are replaced by resin monomers that upon polymerization become micro-

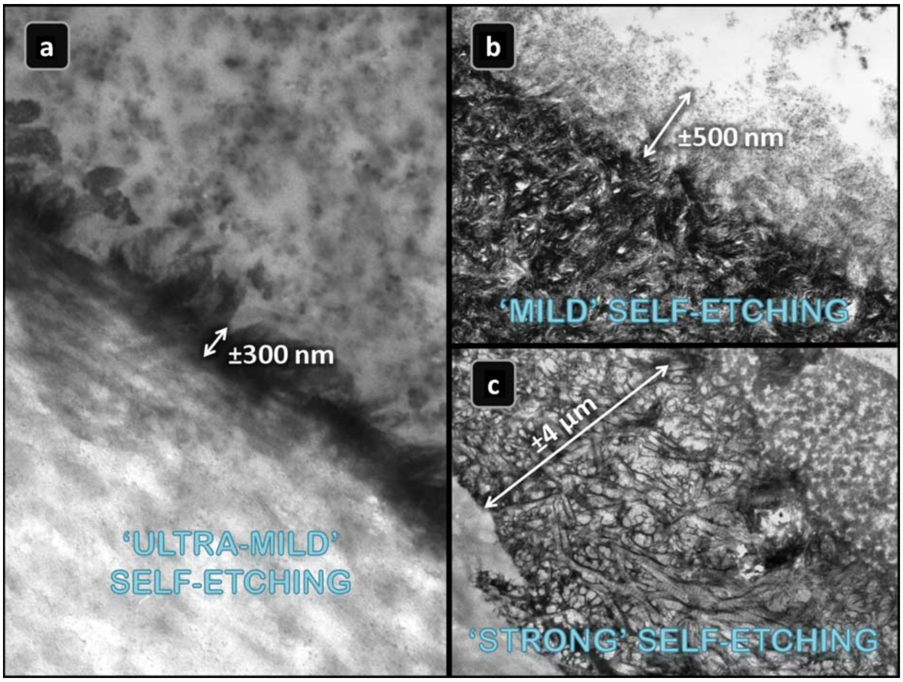

Fig. 1 – Transmission electron microscopy photomicrographs illustrating dentin–adhesive interfaces formed by self-etch adhesives, of which the ultra-structure depends on the interaction of functional monomers with dentin and on the acidity of the self-etching solution. (a) TEM image of a demineralised and stained section, illustrating the very shallow interaction of a so-called 'ultra-mild' self-etch adhesive ($pH > 2.5$). The hybrid layer is approximately 300 nm thick. (b) TEM image of a non-demineralised section. The hybrid layer of a 'mild' self-etch adhesive ($pH \approx 2$) varies between 0.5 and 1 µm. (c) TEM image of a demineralised and stained section. 'Strong' self-etch adhesives ($pH \leq 1$) create a thick, fully demineralised hybrid layer, in which collagen fibrils are no longer protected by hydroxyapatite.

mechanically interlocked in the created porosities [27]. This process, which is called '*hybridization*' on dentin, involves infiltration and subsequent *in situ* polymerization of resin within the created surface porosities, and thus is a process primarily based upon diffusion. While the resultant micro-mechanical interlocking is a prerequisite to achieve good bonding (certainly within clinical circumstances), the potential benefit of additional chemical interaction between functional monomers and tooth substrate components has recently regained attention [28,29]. Additional 'primary' chem-

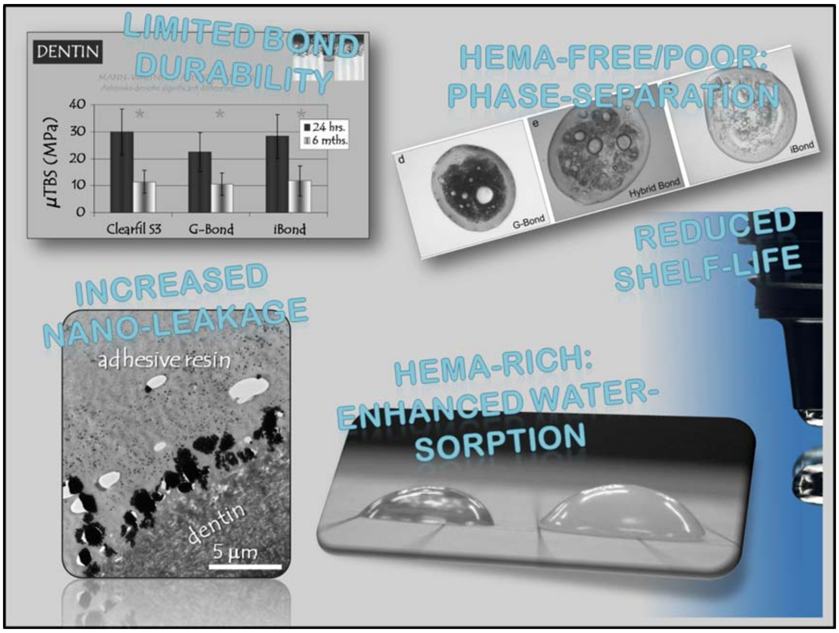

Fig. 2 – The major shortcomings of current one-step adhesives.

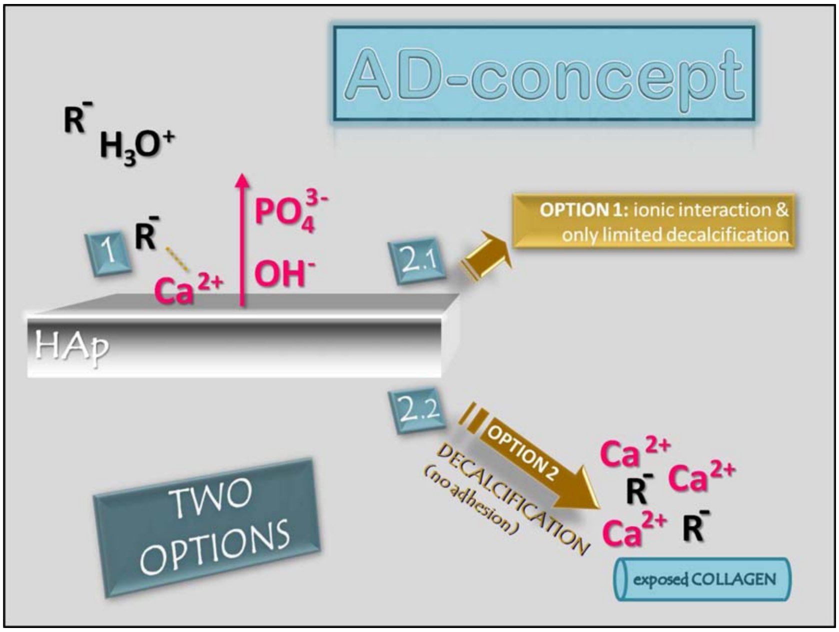

Fig. 3 – Schematic figure of the adhesion–decalcification concept or 'AD-concept'. After ionic interaction of the functional monomer (usually a carboxyl or phosphate group) (PHASE 1), there are two options: either the ionic bond is hydrolytically stable, resulting in a Ca-monomer salt that can co-polymerize with the monomers of the adhesive resin (PHASE 2, OPTION 1 or 2.1), or the ionic bond is not stable, resulting in decalcification and release of calcium and phosphate from the tooth surface (PHASE 2, OPTION 1 or 2.2).

ical interaction is thought to particularly improve bond durability.

The pK_a value of an acid was generally considered as the major parameter that determines how molecules interact with mineralised tissues [11]. However, it does not fully explain the mechanisms why certain molecules adhere to tooth tissue, while others do not, but rather severely decalcify it [30–33]. For instance, 1 M oxalic acid ($pK_1 = 1.27$, $pK_2 = 4.28$) with a pH of 0.6 is more acidic than 10% maleic acid ($pK_1 = 1.94$, $pK_2 = 6.23$), which has a pH of 0.9. Nevertheless, oxalic acid chemically bonds to hydroxyapatite (HAp), while maleic acid decalcifies it. In other words, it is not necessarily true that the lower the pH (the more acidic), the more the solution will demineralise enamel and dentin.

The way molecules interact with HAp-based tissues has been described in the so-called 'AD-concept' or 'Adhesion-Decalcification concept' (Fig. 3) [30,31,34]. This model shows that initially all acids chemically (ionically) bond to calcium of HAp (PHASE 1). This first bonding phase goes together with release of phosphate ($PO_4{}^{3-}$) and hydroxide (OH^-) ions from HAp into the own solution, such that the surface remains electro-neutral. Whether the molecule will remain bonded (PHASE 2, OPTION 1 or 2.1) or will de-bond (PHASE 2, OPTION 2 or 2.2), depends on the stability of the formed bond to Ca, or in other words on the stability of the respective calcium salt.

More specifically, molecules like 10-methacryloyloxydecyl dihydrogen phosphate or 10-MDP (as functional monomer in self-etch adhesives), but also polyalkenoic acids (as functional polymer in glass-ionomers), will chemically bond to Ca of HAp (thus according to AD-concept (PHASE 2, OPTION 1 or 2.1), forming stable calcium-phosphate and calcium-carboxylate salts, respectively, along with only a limited surface-decalcification effect. 'Mild' self-etch adhesives and glass-ionomers indeed only superficially interact with enamel and dentin, and hardly dissolve HAp crystals, but rather keep them in place (within a thin submicron hybrid layer; see below and Fig. 1b).

On the contrary, molecules like phosphoric and maleic acid, but also functional monomers of self-etch adhesives like 2-(methacryloyloxyethyl)phenyl hydrogenphosphate (phenyl-P) and HEMA-phosphates, will initially bond to Ca of HAp (PHASE 1), but will readily de-bond (thus according to 'AD-concept PHASE 2, OPTION 2 or 2.2'). The negatively loaded phosphate ions (or carboxyl groups for carboxyl-based monomers/acids) will remove the positively loaded (and thus electro-statically attracted) Ca ions from the surface, up to a certain depth depending on the application time. This results in a severe decalcification or '*etching*' effect, as it is best known for phosphoric acid that is used as '*etchant*' as part of the '*etch-and-rinse*' approach. Because the calcium-phosphate/carboxylate bond originally formed (during PHASE 1) at the enamel/dentin surface is not stable, the bond will dissociate, leading to a typical etch pattern at enamel and a relatively deep (3–5 μm) hybrid layer at dentin that does no longer contain any HAp crystals (Fig. 1c).

5. Avoid 'strong' self-etch adhesives

'Strong' self-etch adhesives present rather deep demineralisation effects at both enamel and dentin (Fig. 1c). The interfacial ultra-structure produced by these adhesives resembles that of etch-and-rinse systems, but differs for the fact that the dissolved calcium phosphates are not rinsed away. These embedded calcium phosphates are expected to be very unstable in an aqueous environment, thereby seriously weakening the interfacial integrity. Laboratory as well as clinical data have undeniably shown that despite their rather reasonable bonding potential to enamel, strong self-etch adhesives generally underperform at dentin, in particular with regard to bond durability and restoration longevity [35–37]. These data corroborate the AD-concept [30,31], and should be attributed to the low hydrolytic stability of the embedded calcium phosphates, along with the lack of stable chemical interaction with the exposed collagen.

Although manufacturers have introduced strong self-etch adhesives some years ago, especially with regard to their better etching performance at enamel, their severely compromised bonding to dentin has apparently pushed them today more toward the more promising 'mild' self-etch approach.

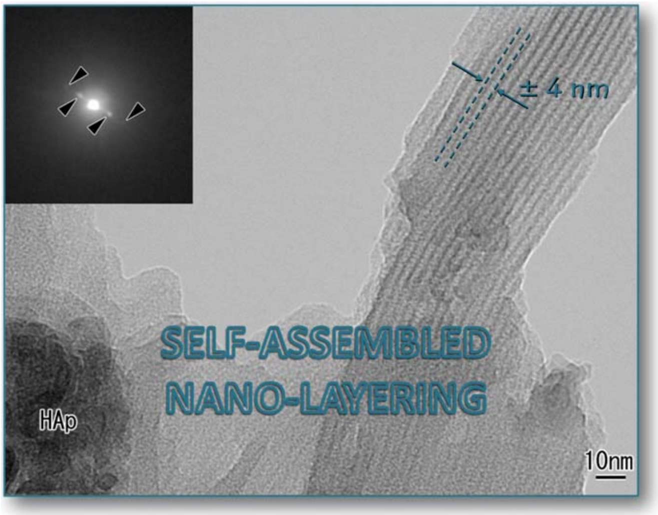

Fig. 4 – This high-resolution TEM image shows the formation of a self-assembled nano-layered structure on synthetic hydroxyapatite, that consists of 4-nm layers and is typically formed by 10-MDP. Each one of these layers consists of two 10-MDP monomers, that have assembled with their methacrylate groups directed toward each other and their phosphate groups directed away from each other.

6. Importance of keeping hydroxyapatite at the interface to protect collagen and generate chemical interaction receptiveness

Indeed, 'mild' self-etch adhesives demineralise dentin only partially, leaving a substantial amount of HAp-crystals around the collagen fibrils (Fig. 1b). Dentinal collagen exposed by an etch-and-rinse procedure has been documented to be highly vulnerable to hydrolytic and enzymatic degradation processes [38–40]. Smart biomimetic remineralisation procedures have been developed by Tay and Pashley [41–44] to 'repair' the natural HAp-protection of collagen. However, the clinical applicability of such a time-consuming process is today still unclear. As a potential remedy to remineralise caries-affected dentin lesions, this procedure appears technologically more rapidly attainable to work intra-orally. Actually, the fact that an etch-and-rinse hybrid layer can be demineralised, confirms the relatively permeable nature of the resin-impregnated collagen layer and perhaps its consequent instability on the long term. On the other hand, it also underlines the great advantage of mild self-etch adhesives as they keep collagen not only encapsulated and thus protected by HAp, but also provide the potential to chemically interact with HAp [27,29].

The resultant two-fold micro-mechanical and chemical bonding mechanism of mild self-etch adhesives closely resembles that of glass-ionomers [27,45]. The latter also typically present with a submicron hybrid layer that still contains substantial HAp that was not dissolved by the polyalkenoic acid. In this respect, glass-ionomers could even be regarded as a kind of mild self-etch adhesives. According to the AD-concept [28,30], polyalkenoic acid is a polymer with a multitude of carboxyl functional groups that as chemical 'hands' grab individual Ca-ions along the mineral substrate. This chemical bonding, combined with micro-mechanical interlocking through shallow hybridization, establishes the unique self-adhesiveness of glass-ionomers (even without any form of beforehand treatment). Glass-ionomers have indeed been recorded with the lowest annual failure rate with regard to Class-V adhesive restorations [1,26]. The basic difference with 'true' resin-based self-etch adhesives is that the latter possess functional monomers with usually only one or two functional chemical groups with affinity to HAp. They provide individual monomers that become upon polymerization a polymer that is linked to HAp, versus glass-ionomers that make use of an already existing (polyalkenoic-acid) polymer with multiple functional groups that are attached to the polymer backbone and can 'grab' Ca at different and remote sites. The additional chemical bonding provided by glass-ionomers and mild self-etch adhesives is believed to be advantageous in terms of bond durability [46,47].

In case of self-etch adhesives, chemical interaction is achieved through specific functional monomers, such as 10-MDP, 4-MET (or 4-methacryloxyethyl trimellitic acid) and phenyl-P. The ionic bond formation of the carboxylic/phosphate groups of these functional monomers to Ca of HAp was first proven by Yoshida et al. in 2004 using XPS (or X-ray photo-electron spectroscopy) [29]. However, chemical bonding potential on its own is insufficient; the formed ionic bonds should also be stable in an aqueous environment. In this sense, the chemical bonding promoted by 10-MDP is not only more effective, but also more stable in water than that provided by 4-MET and phenyl-P, in this order [29]. The dissolution rate of the respective calcium salts of these three monomers, as measured by AAS (or atomic absorption spectroscopy), was inversely related to their chemical bonding potential, as revealed by XPS: the more intense the chemical bonding potential, the less the resultant calcium salt could be dissolved.

Confirming these experimental chemical data (and hence the AD-concept [30,31]), the bond strength to dentin of the 10-MDP-based 'mild' two-step self-etch adhesive Clearfil SE (Kuraray) remained high after long-term thermo-cycling, while that of Unifil Bond (GC) that contains 4-MET, sig-

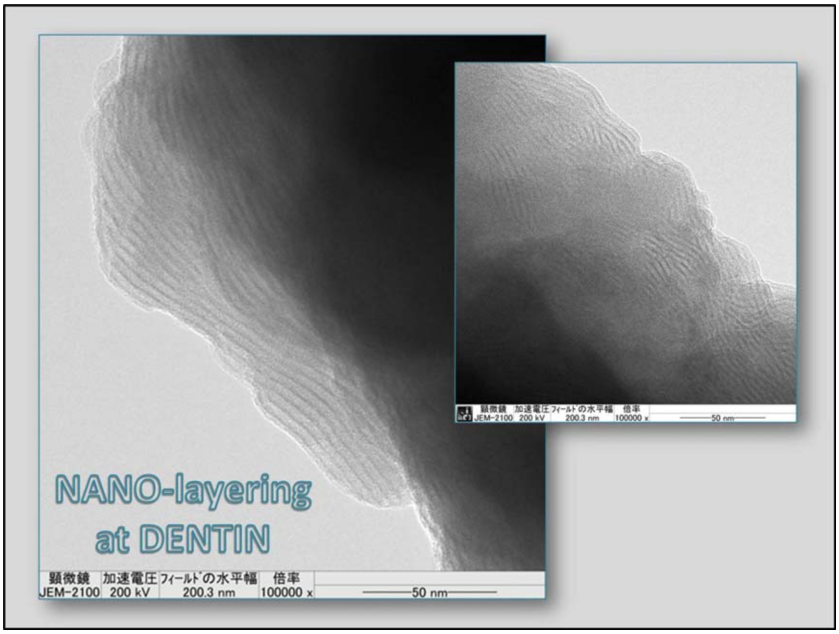

Fig. 5 – Even though hydroxyapatite in dentin differs chemically from pure hydroxyapatite and contains impurities, a similar nano-layering by 10-MDP could be observed by high-resolution TEM on dentin.

nificantly dropped (but only after 100,000 cycles) and that of Clearfil Liner Bond II (Kuraray) that contains phenyl-P, gradually decreased the longer the bond was exposed to thermo-cycling [46]. Clearfil SE Bond (Kuraray) has been proven to yield reliable results in terms of bonding effectiveness and durability when compared to other commercially available self-etch adhesives, this in laboratory as well as clinical research [48–52].

The functional monomer 10-MDP bonds through its phosphate groups to HAp and peculiarly forms a regularly layered structure at the HAp surface (Fig. 4) [29,53]. Both XRD (or X-ray diffraction) of HAp powder allowed to interact with 10-MDP, and high-resolution TEM (or transmission electron microscopy) of 10-MDP-treated HAp powder revealed the formation of a 4-nm layered structure (Fig. 4). Such 'nano-layering' could not be detected for the functional monomers phenyl-P and 4-MET. Each layer of this self-assembled nano-layered structure consists of two 10-MDP molecules with their methacrylate groups directed toward each other and their functional hydrogen phosphate groups directed away from each other [53]. In between the layers, calcium salts are deposited. This high chemical affinity of 10-MDP to HAp along with nano-layering was first demonstrated on pure synthetic HAp using XRD and later confirmed by NMR (or nuclear magnetic resonance). Apatite in natural dentin is carbonated and also contains trace amounts of Na, Mg, Sr, and Al among others [54]. Direct evidence of the formation of a nano-layered structure on natural dentin was later provided by TEM (Fig. 5), and structurally by XRD of 10-MDP-treated dentin samples (Fig. 6) [53]. More recent experiments [55] proved that nano-layering was formed at dentin when an experimental 10-MDP-based adhesive (as well as the commercially available Clearfil SE Bond of Kuraray) was applied to dentin following a clinically relevant application procedure (i.e. 20-s application followed by gently air-drying). Furthermore, rubbing the primer solution on the dentin surface intensified the nano-layering, which may explain why this 'active' application technique increases the bond strength as observed in previous studies. However, nano-layering was clearly less detectable by XRD at enamel, which may be due to the significantly higher crystallinity of enamel, reducing the interaction potential of 10-MDP. Dentinal HAp has not only a lower crystallinity, but also the crystal rods are smaller in size and oriented crisscross (versus parallel oriented at enamel).

While nano-layering and ionic interaction of 10-MDP with Ca of HAp readily occurs, only at a later time some limited deposition of dicalcium phosphate dihydrate or DCPD ($CaHPO_4 \cdot 2H_2O$) was detected, correlatively using NMR and XRD [53,55]. As mentioned before, this chemical interfacial interaction of 10-MDP corresponds to the 'AD-concept PHASE 2, OPTION 1 (or 2.1)' profile, but contrasts to that of phenyl-P that readily resulted in DCPD deposition, confirming the 'AD-concept PHASE 2, OPTION 2 (or 2.2)' profile of phenyl-P. The two functional monomers phenyl-P and 10-MDP should be regarded as the two extremes: phenyl-P rather 'etches', while 10-MDP rather 'bonds' to HAp (with 4-MET behaving somewhat in between).

Comparative interfacial TEM data revealed a slightly thicker hybrid layer for the phenyl-P-based adhesive Clearfil Liner Bond 2 (Kuraray) than that produced by the 10-MDP-based Clearfil SE Bond (Kuraray) (Fig. 7). Moreover, HAp remained abundantly within the hybrid layer of Clearfil SE Bond, but not within that of Clearfil Liner Bond 2, where unprotected collagen was clearly exposed. 'Etching' by phenyl-P was associated with more substantial/rapid DCPD deposition, while 'bonding' by 10-MDP was represented by the formation of a Ca-monomer nano-layered structure. Although for phenyl-P some small XRD-peaks, representing ionic bond-

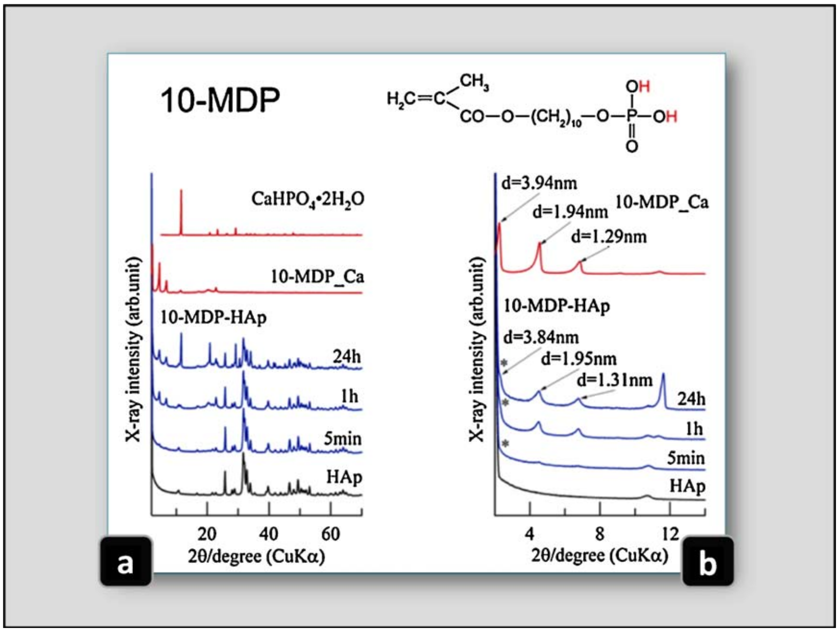

Fig. 6 – Powder XRD spectra showing the interaction of 10-MDP with synthetic hydroxyapatite (a: wide angle; b: low angle).

ing to HAp, were initially also detected, they could not be observed in 24 h samples [53,55]. This again indicated that this Ca-phenyl-P bonding was not stable. In contrast to an etch-and-rinse procedure, the formed DCPD will not be rinsed away following a self-etch procedure, but will be embedded in the hybrid layer, thereby protecting collagen less than natural HAp and thus making the bond more vulnerable to biodegradation. The functional monomer 4-MET interacts somewhat in between the interaction profiles of 10-MDP and phenyl-P, with clearly a higher chemical interaction potential than phenyl-P, but lower than 10-MDP.

The important finding that the adhesive performance of a self-etch adhesive depends on the functional monomer included in the adhesive solution and its particular molecular structure and affinity to HAp, was confirmed by another study, in which the chemical interaction of the three experimental Ivoclar-Vivadent (Schaan, Liechtenstein) phosphonate monomers, 2-[4-

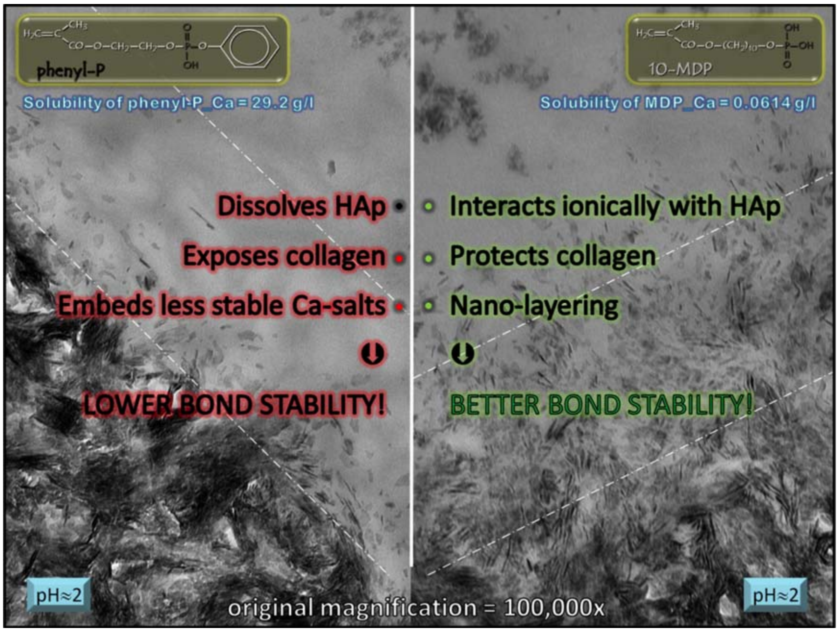

Fig. 7 – TEM images (non-demineralised sections) of the interaction of a phenyl-P-based adhesive (Clearfil Liner Bond 2, Kuraray) and a 10-MDP-based adhesive (Clearfil SE, Kuraray) with dentin. Due to the hydrolytic instability of the phenyl-P–Ca salt, this monomer rather demineralises dentin, whereas 10-MDP remains bonded to hydroxyapatite, resulting in much less demineralisation.

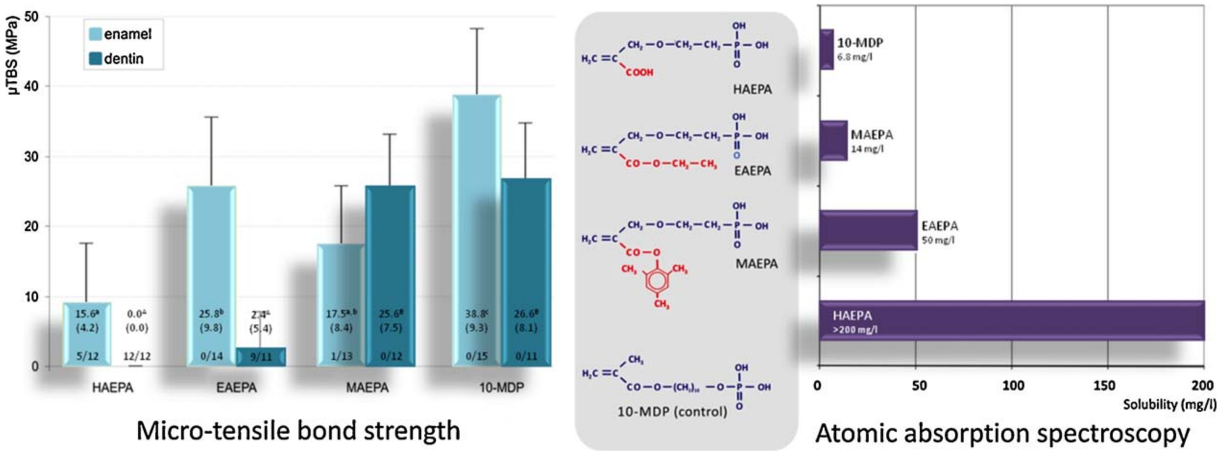

Fig. 8 – A study with experimental monomers confirmed that the chemical bonding capacity of functional monomers to calcium in hydroxyapatite co-determines the adhesive performance of adhesives. (left) The bond strength of three experimental phosphonate monomers synthetized by Vivadent-Ivoclar (Schaan, Liechtenstein: 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate or HAEPA, ethyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate or EAEPA, and 2,4,6 trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate or MAEPA), was assessed and compared to that of 10-MDP as control. In terms of bonding effectiveness, MAEPA proved to be most effective and only at enamel, a significantly lower bond strength was measured as compared to 10-MDP. (right) Good bonding effectiveness corresponded to a low solubility of the respective Ca-salt.

(dihydroxyphosphoryl)-2-oxabutyl]acrylate or HAEPA, ethyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate or EAEPA, and 2,4,6 trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate or MAEPA, was assessed and compared to that of 10-MDP as control [47]. The carboxyl group in HEAPA was esterified in EAEPA and MAEPA with an ethyl- and a phenyl-group, respectively (Fig. 8). Bond strength of experimentally prepared adhesive cements that differed only for the functional monomer, was inversely related to the dissolution rate of the calcium salt of the respective functional monomer (Fig. 8a and b). The latter is according to the AD-concept suggestive of a high chemical bonding capacity following a 'PHASE 2, OPTION 1 (or 2.1)' profile. Only a slightly higher dissolution rate was recorded for MAEPA than for the 10-MDP control, while the 10-MDP-based adhesive cement showed only a significantly higher bond strength to enamel. Ca-HAEPA was highly hydrolytically sensitive, while also the Ca-salt of EAEPA was significantly more soluble than the Ca-salts of MAEPA and 10-MDP. Their respective bonding effectiveness to dentin was correspondingly significantly lower. Recent XRD confirmed that MAEPA formed hydrolytically stable Ca-monomer salts that remained attached to the dentin surface despite rinsing [56]. EAEPA also ionically bonded to Ca at dentin, but the formed Ca-EAEPA salt did not resist washing with ethanol and water. Finally, no evidence for the formation of Ca-HAEPA salt was detected by XRD.

Despite the high chemical interaction potential of 10-MDP and the related nano-layering, a recent finding showed that the application of an experimental 10-MDP:EtOH:H_2O self-etching primer followed by the bonding agent of the commercially available Clearfil SE Bond (Kuraray) did not suffice to reach a bond strength comparable to that of the complete Clearfil SE Bond system (using also the commercially available 10-MDP-based self-etching primer) [55]. When however camphorquinone (CQ) was added as photo-initiator to the experimental 10-MDP:EtOH:H_2O self-etching primer, an equally high bond strength to dentin was measured like that of Clearfil SE Bond (of which the self-etching primer also contains CQ). This finding highlights the need for adequate polymerization, hypothetically thought to be very important in case nano-layering produces a relatively thick intermediary layer. This layer can only polymerize and thus resist de-bonding during bond-strength testing when sufficient photo-initiator is provided locally. Adding CQ to the subsequently applied bonding agent of Clearfil SE Bond appeared insufficient, most likely because of the less penetrable nano-layering arrangement.

In summary, all the above data support the AD-concept [30,31], which prescribes that stable ionic-bond formation to HAp competes with the deposition of less stable calcium-phosphate salt deposition (DCPD). For durable bonding, Ca-monomer salt formation should precede/exceed DCPD deposition.

7. Importance of the smear layer on dentin

It is well known that during cavity preparation using rotary instruments, the surface to bond to will be covered by a smear layer [57,58]. Depending on the preparation technique, this smear layer varies significantly in size and structure. Unfortunately, the smear layer is not attached firmly to the tooth surface, and self-etch adhesives should be able to dissolve it to obtain a satisfactory bond to the underlying tooth surface [59].

There are indications that the bonding effectiveness of especially (ultra-)mild self-etch adhesives may be impaired by thick smear layers [60,61]. In addition, a recent study revealed that a mild self-etch adhesive failed predomi-

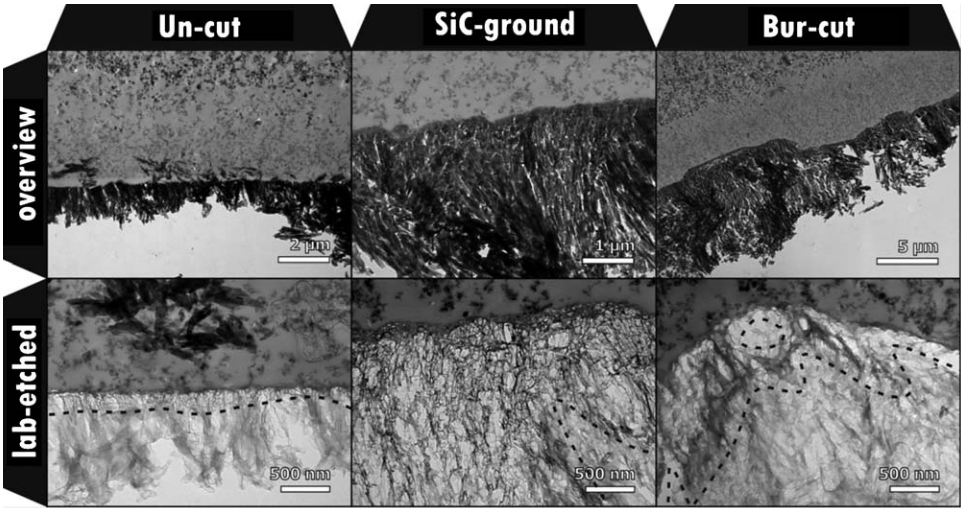

Fig. 9 – Transmission electron microscopy photomicrographs of Clearfil S^3 Bond (Kuraray) bonded to enamel that was prepared in three different manners: (1) solely pumiced (uncut, not prepared by bur), (2) ground by 600-grit SiC-paper, and (3) prepared by a coarse diamond bur. By demineralising (lab-etching) the sections [71], the actual depth of interaction could be evaluated more precisely (images at bottom).

nantly under the hybrid layer after water-aging, which may also be the result of insufficient smear removal by current mild self-etch adhesives [62]. These studies highlight the importance of the cavity-preparation method. It is clear that the main challenge for current self-etch adhesives is to dissolve the smear layer without demineralising the tooth surface too profoundly, thereby removing hydroxyapatite at the interface. Preserving hydroxyapatite at the interface not only protects the collagen from external chemical aggression, but the hydroxyapatite will also provide calcium for chemical bonding to the functional monomer.

8. Self-etching enamel

At enamel, an etch-and-rinse approach using phosphoric acid remains the choice of preference, since it not only guarantees the most durable bond to enamel, but also seals and thus protects the more vulnerable bond to dentin against degradation [48,63–67]. As mentioned above, while ‘strong’ self-etch adhesives generally perform not that unfavorably at enamel, bonding of ‘mild’ self-etch adhesives to enamel (and certainly to unground, aprismatic enamel) remains so far unsatisfactory [48,63,64,68] (Fig. 9). Clinical research has clearly revealed that marginal defects at the enamel margins of a composite restoration develop rather rapidly, whereas the dentin margins appear to maintain their marginal integrity much longer [69,70].

This is somewhat odd considering that the chemical bonding potential of functional monomers to HAp (at least with certain functional monomers) should also be beneficial for the bonding effectiveness to enamel that contains even more HAp than dentin does. Recent XRD analysis of interfacial interaction of 10-MDP revealed significantly more intense nano-layering at dentin than at enamel, both enhanced when the experimental 10-MDP-based self-etching primer was actively rubbed on the surface [55]. Since the nano-layering formed at enamel was not relatively thick, adding CQ to the experimental self-etching primer appeared not necessary (in contrast to bonding to dentin, see above) to reach a bond strength to enamel equally as that achieved by the commercial Clearfil SE Bond system.

More recent research investigated to which extent the compromised enamel bonding obtained with (ultra-)mild self-etch adhesives could be attributed to interference of bur debris smeared across enamel during cavity preparation. Somewhat surprisingly, very little information is available on the morphology of enamel smear-layers. In this respect, we recently ultra-structurally studied the interaction of the so-called

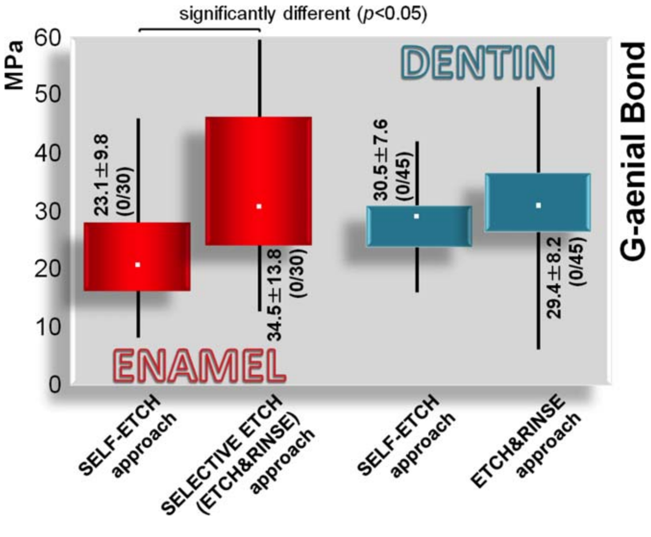

Fig. 10 – Micro-tensile bond strength of the ‘mild’ self-etch adhesive G-aenial Bond (GC) to enamel and dentin using a ‘full’ self-etch approach and a ‘selective’ enamel-etch approach.

‘ultra-mild’ self-etch adhesive Clearfil S^3 Bond (Kuraray) with enamel that was prepared in three ways (Fig. 9) [68], either solely pumice-cleaned and kept un-cut (1), ground using #600-grit silicone-carbide paper (2), or cut using a medium-grit (100 μm) diamond bur (3). At un-cut enamel, the thin aprismatic enamel layer acted as a barrier, which hindered in most areas the adhesive to infiltrate beyond (even though a void-free interface was observed). This aprismatic layer was removed by SiC-paper grinding that enabled the adhesive to penetrate deeper and more uniformly, reaching a firmer micro-mechanical interlock with the formation of a fine reticular resin network. Bur preparation, on the other hand, resulted in a much rougher surface, with numerous subsurface cracks that served as infiltration ‘highways’. A fine reticular mesh, as seen on enamel prepared with SiC-paper, was however not formed, though the bond to enamel must have been stabilised better than when the adhesive was bonded to un-cut enamel.

Altogether, the lower bonding effectiveness of (ultra-)mild self-etch adhesives to enamel should be ascribed most likely in the first place to less potential for micro-mechanical interlocking (which requires some kind of etching), but also to a lower chemical reactivity (nano-layering in case of 10-MDP) with enamel HAp.

Therefore, selective etching of enamel margins with phosphoric acid (Fig. 10), basically turning a two-step self-etch into a three-step adhesive (and a one-step adhesive into a two-step adhesive), is highly recommended to combine a more favorable etch-and-rinse treatment at enamel with a mild self-etch approach that appears to provide better long-term perspectives at dentin. This combined adhesive protocol indeed has already been applied clinically with much success [2].

9. Conclusion

Further optimization of the self-etch approach is achievable by synthesis of functional monomers tailored to exhibit good chemical bonding potential following a mild self-etch approach. This approach appears to guarantee the most durable bonding performance at dentin provided that it deals adequately with the debris smeared across the surface by bur. Micro-mechanical interlocking is still the best strategy to bond to enamel. Selective phosphoric-acid etching of the enamel cavity margins is therefore today highly recommended, followed by applying a mild self-etch procedure to both the beforehand etched enamel and (unetched) dentin. Such mild self-etch adhesive should contain functional monomers with a high chemical affinity to HAp. Phosphoric-acid etching of dentin could nowadays be considered too aggressive for dentin, given all the consequences related to exposure of the vulnerable collagen.

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