Extension of a one-step self-etch adhesive into a multi-step adhesive

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Summary
One-step self-etch adhesives are undoubtedly the most user-friendly adhesives, but have been associated with lower bonding effectiveness as compared to two-step and three-step adhesives. Conversion of a one-step self-etch system into a two-step self-etch adhesive by adding a bonding step, or into a three-step etch&rinse adhesive by adding a beforehand etching step and a bonding step might be tempting in order to improve bond strength.

Objectives: The objective of this study was to investigate whether adding application steps influences the bond strength of a one-step self-etch adhesive.

Methods: In this study, the bonding effectiveness of two experimental one-step self-etch adhesives and three different commercial adhesives to enamel and dentin was determined using a micro-tensile bond-strength protocol. This procedure was repeated for the experimental adhesives transformed into two-step self-etch and three-step etch&rinse adhesives. In addition, their interaction with tooth tissue was investigated using TEM and Feg-SEM.

Results: Transforming a one-step into a two-step self-etch adhesive did improve the bond strength to enamel and dentin, though not significantly. By adding a preceding etching step, the bond strength to enamel was significantly improved, but that to dentin was decreased considerably. The latter must be attributed to hampered resin infiltration of the one-step self-etch adhesive within the relatively deeply exposed collagen fibril network.

Significance: Additional application of a hydrophobic bonding agent slightly improved bonding effectiveness. Adding a preceding etching step is beneficial for enamel but should be avoided for dentin as this will decrease bond strengths, and may even jeopardize the bonding durability.

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Introduction

Current adhesive research focuses on the simplification of application procedure [1]. Reduction of the number of application steps should reduce manipulation time, and abate technique sensitivity, thus improving bonding effectiveness. This trend in adhesive dentistry has led to the introduction of self-etch adhesives, of which the one-step self-etch adhesives (1-SEAs) or the so-called all-in-one adhesives are the most user-friendly adhesive systems nowadays on the market. Their application procedure involves a single step, combining etching, priming and bonding [2,3].

Research, however, so far has demonstrated that simplified systems do not bring the expected improvement in bonding effectiveness, in spite of their assumed reduced technique-sensitivity. Several authors have reported lower bonding effectiveness for simplified adhesive systems [4–9]. Moreover, 1-SEAs in particular have been associated with considerable shortcomings. Tay et al. [10–13] have demonstrated that polymerized 1-SEAs are porous structures that can act as semi-permeable membranes after polymerization, permitting bi-directional water movement across the adhesive layer if not lined by a cured composite. Nanometer-sized voids in the adhesive layer, revealed by silver tracer, are suspected to function as water ducts. Reticular patterns of nanoleakage, so-called water-trees, have been observed in the adhesive layer of 1-SEAs and are considered as sites of incomplete water removal and sub-optimally polymerized resin [14]. Concern about accelerated degradation of the tooth-resin bonds of these adhesives exists, as this permeability may increase the hydrolytic degradation and leaking of resin components [15–17]. More recently, complex processes of phase separation have been shown to occur in one-component HEMA-free 1-SEAs [18]. This phase separation leads to the formation of multiple water droplets that can become entrapped in the adhesive layer upon light curing.

Van Meerbeek et al. [1,19] have proposed a classification of contemporary adhesives, based on the adhesion strategy and application procedure. As differences regarding bonding effectiveness have been found between different adhesive categories, this classification can also serve as a qualitative classification of adhesives. In general, 3-step etch&rinse adhesives (3-E&R) have been found to perform better than 2-step etch&rinse adhesives (2-E&R); similarly, research has reported better results for two-step self-etch adhesives (2-SEAs) than for 1-SEAs [4–6,9]. Regarding durability, a rapid decline in bonding effectiveness has been reported for simplified adhesives [20–22], and these findings are also confirmed by a recent review concerning clinical effectiveness of adhesives [23].

The objective of this study was to investigate whether the bonding effectiveness of a 2-SEA consisting of a 1-SEA followed by a hydrophobic bonding, and of a 3-E&R consisting of the same 1-SEA preceded by an etching step and followed by a hydrophobic bonding is comparable to that of commercial 2-SEAs and 3-E&Rs, and whether adding application steps influences the bond strength. Therefore, the bonding effectiveness of two experimental 1-SEAs applied according to different application procedures and three commercial adhesives (one 1-SEA, one 2-SEA and one 3-E&R) was tested using a micro-tensile bond-strength (μTBS) protocol. The interaction of the adhesives with dentin was comparatively characterized using transmission electron microscopy (TEM) and scanning electron microscopy (Feg-SEM). In addition, the effect of acetone or ethanol used as solvent was investigated in the experimental 1-SEAs.

Material and methods

This study involved two experimental 'mild' 1-SEAs (exp-Eth and exp-Ac) containing both a carboxylate and phosphate-based functional monomer (Table 1) [1]. Both adhesives had a similar composition, but differed in solvent (ethanol and acetone, respectively). Their application procedure involved strong air-drying before light curing.

By adding a hydrophobic bonding agent (UB; from Unifil Bond, GC, Tokyo, Japan) after the application of exp-Eth or exp-Ac (which was not light-cured, thereby serving as a self-etching primer), experimental 2-SEAs were formed (2-SEA/exp-Eth and 2-SEA/exp-Ac). Similarly, by adding a preceding etching step with 35% H3PO4 (Scotchbond etchant, 3M ESPE) and the same hydrophobic bonding agent, 1-SEAs were transformed into three-step etch&rinse adhesives (3-E&R/exp-Eth and 3-E&R/exp-Ac).

As a control group, commercial adhesives representing 1-SEAs (iBond; Heraeus-Kulzer, Hanau, Germany), 2-SEAs (Clearfil SE Bond;
| Table 1 List of adhesives investigated along with their composition and application procedure. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Adhesive**                     | **Class**       | **Manufacturer** | **Composition** | **Application**  |
| Experimental adhesives           | exp-Eth         | GC, Tokyo, Japan | 4-MET, phA-m, DMA, ethanol, water, filler, photoinitiator, stabilizer (pH~2) | Apply adhesive to the entire surface with a disposable applicator. Keep dentin wet (shiny surface) with adhesive for at least 10 s; Strongly air-dry. Light-cure for at least 10 s. Idem as above. |
|                                | exp-Ac          | 1-SEA           | 4-MET, phA-m, DMA, acetone, water, filler, photoinitiator, stabilizer (pH~2) | Apply adhesive to the entire surface with a disposable applicator. Keep dentin wet with adhesive for at least 10 s; strongly air-dry. Light-cure for 20 s. Idem as above. |
|                                | 3-E&R/exp-Eth   | 3-E&R           | Etchant: 35% phosphoric acid. Primer and bonding: see 2-SEA/exp-Eth | Apply three layers of adhesive; wait for 30 s, while slightly agitating. Gently air-dry for few seconds. Light-cure for 20 s. Apply primer for 20 s; gently air-dry. Apply bonding agent Light-cure for 20 s. |
|                                | 3-E&R/exp-Ac    | 3-E&R           | Etchant: 35% phosphoric acid. Primer and bonding: see 2-SEA/exp-Ac | Apply three layers of adhesive; wait for 30 s, while slightly agitating. Gently air-dry for few seconds. Light-cure for 20 s. Apply primer for 20 s; gently air-dry. Apply bonding agent Light-cure for 20 s. |
| Control adhesives               | iBond           | 1-SEA           | Heraeus-Kulzer, Hanau, Germany | UDMA, 4-MET, glutaraldehyde, acetone, water, photo-initiator, stabilizer |
|                                | Clearfil SE Bond | 2-SEA           | Kuraray, Osaka, Japan | Primer: 10-MDP, HEMA, hydrophilic DMA, photo-initiator, aromatic tertiary amine, water. Bonding: 10-MDP: Bis-GMA, HEMA, Hydrophobic DMA, photo-initiator, aromatic tertiary amine, silanated colloidal silica |
Kuraray, Osaka, Japan) and 3-E&R adhesives (Optibond FL; Kerr, Orange, Ca, USA) were tested as well.

**μTBS-Testing**

Human third molars (gathered following informed consent approved by the Commission for Medical Ethics of KU-Leuven) were used within 1 month after extraction. They were stored in 0.5% chloramine/water at 4°C until used. To prepare dentin samples, the occlusal crown third was removed with a diamond saw (Isomet 1000, Buehler, Lake Bluff, IL, USA), thereby exposing a flat mid-coronal dentin surface. A bur-cut smear layer was produced by removing a thin layer of the surface using a Micro-Specimen Former (University of Iowa, Iowa City, IA, USA), equipped with a high-speed regular-grit (100 μm) diamond bur (842, Komet, Lemgo, Germany). For enamel, a flat surface was ground using the same bur at the buccal and lingual surface of a tooth. After application of the experimental and control adhesives according to the instructions listed in Table 1, dentin was built up without delay using Gradia Direct Anterior (GC).

After storage overnight in distilled water (37°C), rectangular sticks (2×2 mm wide; 8–9 mm long) were sectioned perpendicular to the adhesive–tooth interface using the Isomet saw. Only the four central sticks were used to eliminate substrate regional variability [24,25]. The sticks were trimmed at the interface into an hourglass shape (diameter of 1.1 mm) using the Micro-Specimen Former, equipped with a fine-grit (30 μm) diamond bur (5835KREF, Komet) in a high-speed handpiece under air/water coolant. The specimens were fixed to Ciucchi’s jig with cyanoacrylate glue (Model Repair II Blue, Dentsply-Sankin, Ohtawara, Japan) and stressed in tension at a crosshead speed of 1 mm/min using a universal testing device (LRX, Lloyd, Hampshire, UK). The μTBS was derived by dividing the imposed force at the time of fracture by the bond area (mm²). When a specimen failed during processing (pre-testing failure), the μTBS was set at 0 MPa [26,27]. One-way ANOVA and the Tukey HSD multiple comparison test were employed to evaluate the statistical differences in μTBS between the different application methods and experimental and control 1-SEAs, 2-SEAs and 3-E&R adhesives (α = 0.05). The mode of failure was determined with a stereomicroscope at 50× magnification.

Representative dentin and composite μTBS-fracture planes, exhibiting the most frequently observed failure mode, and a μTBS close to the mean were processed for field-emission gun
scanning electron microscopy (Feg-SEM; Philips XL30, Eindhoven) using common specimen processing described previously [28].

**TEM interface characterization**

Each adhesive was applied to bur-cut dentin according to the application procedure mentioned in Table 1. The specimens were processed for TEM according to the procedure described in detail by Van Meerbeek et al. [29]. Non-demineralized and lab-demineralized (10% formaldehyde-formic acid for 36 h) ultrathin sections were cut (Ultracut UCT, Leica, Vienna, Austria), and examined unstained and positively stained (5% uranyl acetate for 20 min/saturated lead citrate for 3 min) using TEM (Philips CM10, Eindhoven, The Netherlands). In order to reveal the defects in acid-etched hybrid layers, additional specimens of Optibond FL and 3-E&RM375 exp-Ac stained with 50 wt% ammoniacal silver nitrate solution were prepared according to a nanoleakage detection protocol previously described by Tay et al. [14].

**Results**

The micro-tensile bond strengths of exp-Eth and exp-Ac varied significantly over the three different application protocols (Figs. 1 and 2). With regard to enamel, each additional application step increased the bond strength. However, this increase was significant only when the experimental 1-SEAs were extended to three-step etch&rinse adhesives. For dentin, the bond strength increased when a 2-SEA protocol was followed. This rise in μTBS, however, was not significant. When dentin was etched prior to the application of primer (1-SEA) and bonding (UB), there was a significant drop in bond strength of both exp-Eth and exp-Ac.

Among the control adhesives (Fig. 2), iBond performed significantly worse than the others. On enamel, Optibond FL achieved significantly higher bond strengths than iBond and Clearfil SE Bond. On dentin, however, μTBS of Optibond FL was not significantly different from Clearfil SE Bond. Significant differences were observed between

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Figure 1  Box-whisker plot denoting the mean μTBS (diamonds) and median μTBS (line in bar) to enamel (top) and to dentin (bottom). The bar indicates the lower and upper quartile and the whiskers define minimum and maximum. On the right, the mean μTBSs with standard deviation are shown (mean (standard deviation); n, total number of specimens; ptf, pre-testing failure) to enamel (top) and to dentin (bottom). One-way ANOVA and Tukey HSD multiple comparison test were employed to evaluate statistical differences between the different application methods of exp-Ac and exp-Eth. A separate test was performed for enamel and dentin.
the experimental 2-SEAs and C-SE and between the experimental 3-E&R s and Optibond FL (Fig. 2).

Failure analysis on enamel revealed a predominantly mixed adhesive failure pattern for all adhesives, sometimes involving cohesive fracture of enamel or composite (Fig. 3). 3-E&R/exp-Eth and 3-E&R/Ac exhibited a mixed failure usually involving enamel fracture. As for dentin, all adhesives failed mixed-adhesively, except for 3-E&R/exp-Eth and 3-E&R/Ac, which all failed completely adhesively (Fig. 3).

TEM observations of dentin showed the formation of a hybrid layer with different characteristics for each class of adhesive (Figs. 4-6).
All self-etch adhesives in this study created a hybrid layer with a thickness of 0.5–1 μm, in which hydroxyapatite crystals could still be found (Figs. 4 and 5a–c). When dentin was etched, a hybrid layer of 3 μm that was completely devoid of hydroxyapatite and distinct resin tags was formed (Fig. 5d–f). A similar but overall thicker hybrid layer (5 μm) was produced by Optibond FL (Fig. 6). All tested 1-SEAs showed droplets in their adhesive layers (Fig 4). However, no droplets were found in the 2-SEAs or the 3-E&Rs (Fig. 5). Applying a hydrophobic bonding after application of exp-Eth or exp-Ac enlarged the thickness of the adhesive layer from 10 to 50 μm. After silver-staining, the hybrid layer of 3-E&R/exp-Ac exhibited a spot-like pattern of nanoleakage, whereas Optibond FL intermittently exhibited dense deposits of silver throughout the hybrid layer (Fig. 6).

Discussion

A 1-SEA that can be extended with a corresponding gain in bonding effectiveness would give a dentist in practice the choice between a simplified and a conventional, more elaborate adhesive. Such a universal adhesive could be adapted to the clinical situation (e.g. deciduous teeth, child, available time, etc.) and would eliminate the need for stocking several adhesives. However, the merit of a system that consists of a basic priming solution that can be used both as an individual adhesive and as part of a 2-SEA and 3-E&R depends on the usefulness of adding application steps. This study clearly showed that the tested experimental one-step self-etch adhesives could not be extended without suffering the consequences. Even though the application of a hydrophobic bonding onto the non-cured 1-SEAs yielded higher bond strengths (although not significant) both to enamel and to dentin and a prior etching step significantly increased the bond strength to enamel, the bond strength to dentin was influenced adversely by this preceding etching step. Therefore, the hypothesis that adding an application step improves the bonding effectiveness must be rejected when the bond strength to dentin is regarded, but accepted for bond strengths to enamel.
In this study, no statistical differences were found between the two experimental 1-SEAs adhesives, exp-Eth and exp-Ac (Fig. 1). Even when these adhesives were applied according to a 2-SEA protocol or a 3-E&R protocol, the obtained $m_{TBS}$ was similar within each application group. Any effect of the solvent on the bonding effectiveness was hence excluded. This is in accordance with an earlier study regarding the phase separation phenomenon in these 1-SEAs. This study did show a distinct effect of the solvent on the course of the phase-separation reaction, but no effect on the bond strength [18]. As a consequence, the second part of the null hypothesis stating that there is no difference between use of ethanol or acetone must be accepted. Nonetheless, acetone is preferred as a solvent medium, because of the better hydrolytical stability of the functional monomers in acetone than in ethanol (unpublished data).

HEMA-free 1-SEAs are prone to phase-separation reactions, giving rise to multiple droplets in the adhesive layer, which can get entrapped upon light curing [18]. In order to reduce the number of droplets in the adhesive and to remove water from the adhesive, a strong air-blowing protocol was applied for the two experimental 1-SEAs. TEM and SEM observations revealed that not all droplets had been removed, but their number had been drastically decreased. When iBond was applied according to the manufacturer’s instructions, the adhesive layer also contained droplets.

On enamel, all 3-E&R adhesives obtained higher bond strengths than the self-etch adhesives. However, this increase in bond strength is only significant when compared to the 1-SEAs. The higher bond strengths for acid-etched enamel can be explained by the more micro-retentive enamel surface obtained when enamel is etched with phosphoric acid as compared to when enamel is etched by the self-etch adhesive. The self-etch adhesives in this study belong to the category of mild self-etch adhesives with a pH of approximately 2. Several authors have reported that mild self-etch adhesives only shallowly demineralize enamel, resulting in a very thin micro-retentive pattern without formation of distinct macro- and micro-resin tags [30,31]. This ill-defined etching pattern has been associated with a lower bond strengths [32–35]. An additional factor influencing the bond strength is the short application time, which was

![TEM images of exp-Eth and exp-Ac on dentin](image_url)

**Figure 4** Transmission electron photomicrographs of exp-Eth and exp-Ac on dentin. No morphological difference could be observed between both adhesives. (a) Non-demineralized not-stained TEM showing an overview of the interface of exp-Ac with dentin. Note the distinct oxygen inhibition layer on top of the thin adhesive layer (7–12 μm). Strong air-blowing the adhesive before light curing reduced the number of droplets in the adhesive layer considerably. (b) Non-demineralized not-stained TEM of the hybrid layer created by exp-Ac on smear-layer covered dentin. Dentin was only partially demineralized, and hydroxyapatite crystals remain scattered throughout the shallow (0.5-1 μm) hybrid layer. (c) Non-demineralized not-stained TEM of exp-Eth revealing small droplets in the adhesive layer, in spite of strong air-blowing the adhesive after application. (d) Demineralized, stained TEM of the submicron hybrid layer formed by exp-Eth (Ar, adhesive resin; C, composite; Hy, hybridized layer; O2-I, oxygen inhibition layer; Ud, unaffected dentin).
only 10 s for the experimental adhesives. However difficult to compare, the longer priming time of 20 or 30 s for Clearfil SE Bond and iBond, respectively, did not involve higher bond strengths.

Transforming a 1-SEA into a 2-SEA did yield higher bond strengths although this effect was not statistically significant. Several reasons for this moderate rise in bond strength may be considered.

Figure 5  Transmission electron photomicrographs of 2-SEA/exp-Eth and 2-SEA/exp-Ac (a, b and c); and 3-E&R/exp-Eth and 3-E&R/exp-Ac (d-f) on dentin. (a) Non-demineralized, not-stained TEM of the hybrid layer of 2-SEA/exp-Ac. No droplets could be found in the adhesive layer. The morphological appearance of the hybrid layer is similar to that of exp-Ac, which is consistent. The adhesive layer, however, is much thicker (up to 50 μm) than the one of exp-Ac (not in picture visible). (b) Non-demineralized not-stained TEM of 2-SEA/exp-Eth, showing a partially demineralized hybrid layer. (c) Demineralized, stained TEM of 2-SEA/exp-Ac showing a shallow hybrid layer, similar to that in Fig. 4d. (d) Non-demineralized, not stained TEM giving an overview of 3-E&R/exp-Ac on dentin. A hybrid layer that is characteristic for phosphoric-acid etching is formed and the dentinal tubules are sealed by resin tags. (e) Non-demineralized, not stained TEM of 3-E&R/exp-Ac, showing the hybrid layer of approximately 3 μm, which is rather small for phosphoric-acid etched dentin. After air-drying, the demineralized collagen network collapsed, but exp-Ac must have been incapable of re-expanding it completely. (f) Demineralized, stained TEM of the hybrid layer created by 3-E&R/exp-Eth. Note the accumulation of remaining silica filler particles from the etching gel on top of the hybrid layer, which can also be seen in d and e (Ar, adhesive resin; Hy, hybridized layer; Rt, resin tag; Ud, unaffected dentin).

Figure 6  Transmission electron photomicrographs of 3-E&R/Exp-Ac (left) and Optibond FL (right) on dentin, after silver nitrate staining. (a) TEM of 3-E&R/Exp-Ac on dentin showing a spotted pattern of nanoleakage throughout the whole hybrid layer, which could be seen in all samples. (b) TEM of Optibond FL showing a similar hybrid layer as 3-E&R/Exp-Ac. However, only intermittently, dense deposits of silver were observed in Optibond FL. Whereas some parts of the hybrid layer exhibited nanoleakage (in this image), other locations were devoid of silver-staining (not in this image) (Ar, adhesive resin; Hy, hybridized resin; Rt, resin tag; Ud, unaffected dentin).
The most plausible explanation must be found in the different proportional composition of one-step and two-step adhesives. Although one- and two-step adhesives generally contain the same components (they both contain functional monomers, cross-linking monomers, solvent, inhibitors and activators), the amounts of ingredients applied on the tooth surface differ considerably among one- and two-step adhesives. Whereas 2-SEAs consist of a pure priming solution containing only functional etching monomers dissolved in organic solvent and water, and a solvent-free bonding containing hydrophobic cross-linking monomers (such as UDMA, TEGDMA), 1-SEAs are complex mixtures of both these hydrophobic and hydrophilic ingredients. Usually, one-component 1-SEAs contain acidic functional monomers dissolved in high concentrations of organic solvent and/or water blended with hydrophobic cross-linking monomers. As the solvent and functional monomers usually make up almost 50% of the adhesive, the concentration of hydrophobic monomers is drastically reduced. Since the mechanical strength of the adhesive is mainly provided by the polymerization of cross-linking monomers, relatively less hydrophobic monomers are available on the tooth surface after application of the 1-SEA, which impairs the bond strength [34,36]. When the 1-SEA was applied according to a 2-SEA protocol, the additional application of the hydrophobic bonding must have increased the concentration of the hydrophobic monomers, which explains increased bond strength. In addition, by applying a hydrophobic bonding, the uncured 1-SEA that was applied as primer was diluted, leading to a thicker and more uniform layer with lower concentrations of retained water and solvent. Sites of remaining water and solvents are thought to weaken the adhesive layer [37–40]. Another explanation is the effect of HEMA in the bonding agent on the phase separation in the 1-SEA. When this 1-SEA is not light-cured, HEMA in the bonding counteracts the phase-separation reaction by bringing the adhesive’s ingredients back into solution. This was also confirmed by SEM and TEM showing that 2-SEA/exp-Eth and 2-SEA/exp-Ac did not exhibit droplets in their adhesive layer. As any kind of flaws in the adhesive layer may act as stress raisers, droplets are bound to affect the bond strength adversely [41]. Absence of droplets in the experimental 2-SEAs is likely to lead to higher bond strengths. Furthermore, the beneficial effect of a thicker adhesive layer in the 2-SEAs may also explain the slight increase in bond strength [42,43].

Regarding the bonding effectiveness of Clearfil SE Bond to dentin, this commercial adhesive obtained significantly higher bond strengths than the two custom-made 2-SEAs and than all 1-SEAs. Moreover, Clearfil SE Bond performed equally well as the commercial 3-E&B Optibond FL on dentin. These observations are in agreement with the results of other, both in vitro and in vivo studies [4,9,44–46]. Its good performance on dentin can be explained by its specific and adapted composition and the use of the functional monomer 10-MDP, which has been shown to exhibit high chemical interaction capacity to hydroxyapatite [47].

When dentin had been etched prior to the application of 1-SEA and hydrophobic bonding, a decrease in bond strength was observed. Additional phosphoric acid etching even negated the beneficial effect on the bonding effectiveness of the application of an additional hydrophobic bonding agent. 3-E&B/exp-Eth and 3-E&B/exp-Ac exhibited significantly lower bond strengths than Optibond FL. This drop in bond strength to dentin must be attributed to suboptimal infiltration of the demineralized collagen network and subsequent poor adaptation of the bonding resin to the collagen fibrils. TEM and nanoleakage observations confirmed the formation of an inferior and porous hybrid layer by 3-E&B/exp-Ac. Even though some nanoleakage could be observed locally in the hybrid layer of Optibond FL under the form of dense silver deposits, the whole hybrid layer of Exp-Ac/E&R exhibited a consistent spotted pattern, suggesting a porous hybrid layer that is prone to silver stain uptake (Fig. 6). This pattern is suggestive of inadequate resin infiltration and poorly enveloped collagen fibrils. When the demineralized collagen network is not optimally impregnated, the exposed collagen fibrils are not protected by resin, making them susceptible to tensile forces [48]. On the longer run, hydrolytic breakdown may jeopardize the bonding effectiveness [49]. SEM observations confirmed that failure under tensile stress occurred adhesively at the bottom of the hybrid layer (Fig. 3). The dense silver deposits that can be observed in the hybrid layer of Optibond FL are also an indication for poor resin impregnation and gaps in the hybrid layer, but as their appearance is less prevalent, the bond strength of Optibond FL was probably not influenced to the same extent as the bond strength of 3-E&B/exp-Eth and 3-E&B/exp-Ac.

This suboptimal resin infiltration can be accounted to different causes [50]. As the major function of primer solutions in 3-E&B is to ensure sufficient wetting of the exposed collagen fibrils, a good primer is usually characterized by high wetting properties and by low viscosity and usually contains low-molecular agents, enabling good diffusion [1,49,51]. 1-SEAs in this study that
functioned as primer are filled with filler-particles, rendering their solutions rather viscous. Moreover, as these filler particles are about 20 nm in size, they may hamper good infiltration of the resin into the collagen network with interfibrillar sizes of only 20 nm. These interfibrillar spaces are even smaller when the collagen network has collapsed due to air-drying, as was done in this study [52]. The rather small hybrid layer observed by TEM can be regarded as an indication for collagen collapse (Fig. 5d–f). Whereas the hybrid layer of Optibond FL was approximately 5 μm thick, the experimental 3-E&Rs only yielded a hybrid layer of 3 μm. In order to re-expand the network, a water-containing primer must be applied [19,53]. Even though the 1-SEAs in this study contained water, needed as an ionization medium for the acidic monomers, the collagen network could not be re-expanded as the filler content may also have hindered sufficient water-influx into the demineralized dentin. Probably, the short application time of 10 s of the ‘primer’ in 3-E&R/exp-Eth and 3-E&R/exp-Ac also accounts for the reduced bonding outcome and an adjusted application procedure with longer application time may be requested [50].

Our findings are in concordance to those of other authors, who also observed increased enamel bond strengths but impaired bonding effectiveness to dentin for 2-SEAs preceded by a phosphoric acid etching step [48,54,55]. This study indicates that not only the class into which an adhesive can be classified is an important parameter for bonding effectiveness, but also that the composition of the adhesive must be adapted to the application procedure.

To conclude, transforming the 1-SEAs into 2-SEAs led to slightly improved bonding effectiveness. Adding a preceding etching step is beneficial for bond strength to enamel but should be avoided for dentin as this will not ameliorate bond strengths, and may jeopardize bonding durability.

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References
