Review Article

Role of the smear layer in adhesive dentistry and the clinical applications to improve bonding performance

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ABSTRACT

Currently, dental adhesives can be divided into two systems; a smear layer-removal approach with etch-and-rinse adhesives or a smear layer-modified approach with self-etching adhesives. After phosphoric acid etching, the smear layer is completely removed. More attention is, however, required when using self-etching adhesives. The smear layer is partially demineralized by the weak acidic monomer and subsequently incorporated into the hybrid layer. Therefore, the characteristics of the smear layer play an important role on the bonding performance of self-etching adhesives. Such characteristics, for instance, smear layer thickness and smear layer density, are influenced by many factors, *e.g.*, instruments used for dentin surface preparation, cutting speed, and the abrasive particle size of the cutting instruments. This review discusses the contributing factors that affect the smear layer characteristics, and the influence of the smear layer on the bonding performance of dental adhesives. Also, the application techniques regarding how to improve the bonding performance of self-etching adhesives – the smear layer removal by using chemical agents, or the modification of the adhesive application procedures – are provided.

1. Introduction

Adhesion to enamel and dentin can be divided into an etch-and-rinse approach and a self-etching approach. The etch-and-rinse approach requires a separate step of applying phosphoric acid to demineralize the smear layer and tooth structure. For dentin, after applying 30–40% phosphoric acid, the smear layer is completely removed, and the underlying dentin is demineralized, exposing dentin collagen [1]. The zone of exposed collagen is subsequently infiltrated with resin monomer to form a so-called hybrid layer [2,3]. In contrast, an acidic primer is used in the self-etching approach to demineralize the tooth structure and simultaneously penetrate the underlying dentin. Due to the mild pH of the acidic primer, the smear layer is partially demineralized (Fig. 1a, b). Consequently, the residual smear layer is incorporated into the hybrid layer (Fig. 1c). This structure is called the hybridized smear layer [4], or resin-smear complex [5] in some reports.

It has been reported that the bonding performance of self-etching adhesives is affected by the smear layer, especially with mild- and ultra-mild self-etching adhesives. This unfavorable effect of the smear layer also depends on the instruments used for surface preparation. However, *in vitro* studies have demonstrated that the bond strength of self-etching adhesives can be improved with several bonding modification techniques. This review discusses the smear layer characteristics and their effects on the bonding performance of dental adhesive, including application techniques to improve the clinical outcome.

2. Smear layer definition

Smear layer is a zone of tooth preparation debris found spread on the surface after tooth preparation. Some of this debris blocks the orifices of the dentinal tubules, forming smear plugs that decrease the dentin permeability by 86% [6]. However, the fluid from the dentinal tubules can permeate through the smear layer due to its micro-porous structure [7]. The smear layer is mainly composed of hydroxyapatite and collagen that is denatured by the friction and heat during tooth preparation [8]. It has been suggested that
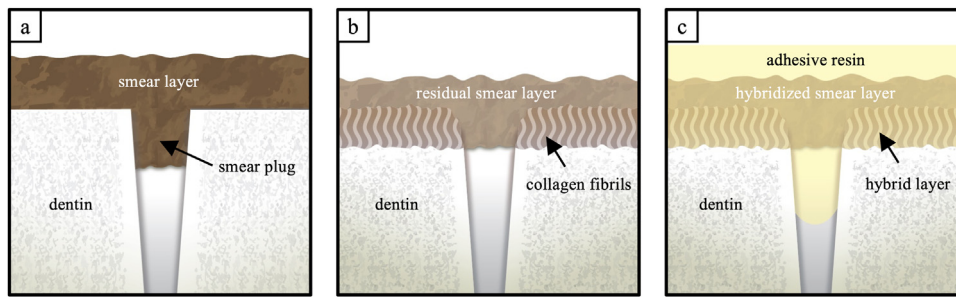
Fig. 1. Schematic diagram of smear layer treated with self-etching adhesive. (a) Smear layer covering dentin surface after tooth preparation. (b) After being treated with self-etching adhesive, the smear layer was partially demineralized and superficial collagen was exposed. (c) After resin polymerization, the residual smear layer was incorporated into hybridized smear layer between the adhesive layer and the hybrid layer.

the smear layer should be removed prior to the application of the bonding agent. Complete removal and partial removal of the smear layer are observed when phosphoric acid is used in etch-and-rinse adhesives and self-etching adhesives, respectively [9,10].

3. Role of the smear layer in dentin bonding

Prior to the use of phosphoric acid, dental adhesives in the early generations bonded directly to the smear-covered surface [8,11]. The *in vitro* bond strengths of these adhesives have been reported to be less than 5 MPa, which could easily result in clinical debonding [8,11]. The debonded specimens were also mainly classified as cohesive failure within the smear layer because the adhesive resin was hydrophobic and, therefore, failed to penetrate through such a zone of debris [12].

3.1. Etch-and-rinse approach

3.1.1. Removing the smear layer with phosphoric acid

It is well accepted that the smear layer can be removed by applying phosphoric acid. However, the appropriate concentration of the acid needs to be carefully considered. Lower concentrations, such as 0.13% and 20%, demonstrated a less aggressive etching effect, and the smear layer has been shown not to be totally removed [9]. Similarly, the high concentration, such as 65% in Super-Bond C&B Red Activator (Sun Medical Co., Ltd., Moriyama, Japan), also demonstrated the inferior demineralization effect [13] and lower bond strength [14]. Clinically, the optimum concentration of phosphoric that is routinely used is 30-40%. With phosphoric acid etching, the smear layer does not affect etch-and-rinse adhesive systems because it is completely demineralized and rinsed away [15]. However, the long-term degradation of dentin collagen has been shown to be more pronounced with etch-and-rinse adhesive compared to that of self-etching adhesive [16]. This phenomenon is possibly due to the aggressive demineralization of phosphoric acid that expose more dentin collagen fibrils. Consequently, matrix metalloproteinases (MMPs), the endogenous enzyme responsible for the collagenolytic activity, are activated and degrade denuded exposed collagen overtime [17].

3.1.2. Alternative etchants

Due to the drawbacks of phosphoric acid, new alternative etchants have become available, *e.g.*, Multi Etchant (Yamakin, Osaka, Japan), Shofu Enamel Conditioner (Shofu, Kyoto, Japan), and an experimental zirconium oxynitrate conditioner (Ivoclar Vivadent, Schaan, Liechtenstein) The compositions and the chemical formula of the active component of each alternative etchant are provided in Table 1. These alternative etchants demonstrated higher dentin bond strength compared with phosphoric acid [18,19]. Moreover, the inhibitory effect of the experimental zirconium oxynitrate conditioner on MMPs has also been demonstrated

[19]. Additional studies are warranted to further evaluate the effects of these new etchants on different smear layer preparations.

3.1.3. Reduced phosphoric acid etching time

Another approach to minimize the dentin collagen degradation caused by phosphoric acid etching is to reduce the etching time. Though it has been proposed that the depth of dentin demineralization was related to the etching time [20,21], no adverse effect on dentin bond strength was observed when the etching time was reduced to 5 s [22]. On the other hand, the bond strength of primary dentin was significantly improved when phosphoric acid etching time was reduced by 50% [23]. Recently, it has been demonstrated that etching with phosphoric acid to dentin for 3 s improved the bond strength and bond durability of universal adhesives [24]. Similar smear layer demineralization pattern after etching with phosphoric acid for 3 s and 15 s has also been observed. It has been stated that shortening the etching time can reduce the adverse effect of phosphoric acid on bond degradation. However, further investigation of the effect of reduced etching time on MMPs activity is needed.
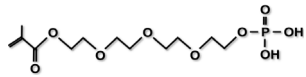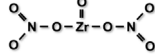
3.2. Self-etching approach

3.2.1. Smear layer modified with self-etching system

When using self-etching adhesive systems, the smear layer characteristics and the etching ability of the adhesives are the two main factors that influence the bonding outcome [10,25–27]. It has been previously mentioned that the smear layer characteristics are critical for dentin adhesion [10]. Many investigations have evaluated the effects of the smear layer produced by different preparation instruments. However, a control group with a smear-free surface was not included for comparison in most studies. Therefore, the effects of the smear layer on dentin adhesion might be underrated. In 2000, a fractured dentin technique was introduced by Tay et al. to compare the bond strength of the self-etching adhesive to smear-free and smear-covered dentin [28]. The results demonstrated that the bond strength of a 2-step self-etching adhesive, Clearfil SE Bond, was not affected by the smear layer created by silicon carbide (SiC) paper [28]. A study by Suyama et al. compared the bond strength on fractured dentin with that on diamond bur-cut dentin [29]. They found that the diamond bur-cut smear layer interfered with the interaction of the self-etching adhesive with the underlying dentin [29]. These studies imply that the smear layers created from different instruments differentially impact the bonding with self-etching adhesives. More details regarding smear layer characteristics are discussed in the next section.

3.2.2. Classification of self-etching adhesives by pH

The etching ability of the self-etching adhesives is related to their pH, which can be classified into strong self-etching adhesives (pH $\leq$ 1), intermediately strong self-etching adhesives (pH 1–2),

Table 1
Compositions and chemical formula of the active component of each alternative etchant.

Product	Manufacturer	Compositions	Chemical formula of the active component
Multi Etchant	Yamakin, Osaka, Japan	Methacryloyl oxytetra ethylene glycol dihydrogen phosphate (M-TEG-P), thickener, colorant	
Enamel conditioner	Shofu, Kyoto, Japan	Three carboxylic acid-based organic compounds (Polyacrylic acid and other 2 smaller molecular weight organic acids), thickener, colorant	
Zirconium oxynitrate conditioner (experimental)	Ivoclar Vivadent, Schaan, Liechtenstein	$ZrO(NO_3)_2$, water, glycerol, fumed silica, polyethylene oxide	

mild self-etching adhesives (pH ~2), and ultra-mild self-etching adhesives (pH > 2.5) [25]. Typically, an adhesive with a lower pH tends to demonstrate better etching ability. However, it has been suggested to avoid using strong self-etching adhesives [25]. The etching pattern of the strong self-etching adhesives is similar to that of phosphoric acid; however, the difference is that the dissolved mineral content is not rinsed away. Therefore, the dentin bond can be weakened by the remnants of the dissolved minerals. In contrast, the mild self-etching adhesives superficially demineralize the dentin surface. The hydroxyapatite remnants are still available for chemical bonding, especially with 10-MDP monomer to form 10-MDP calcium salts [25,30]. This structure is responsible for the long-term durability of the resin-dentin interface [30]. Therefore, using mild self-etching adhesives is preferable. However, with their weak acidity, the buffering effect of the smear layer should be taken into account [26,31,32].

3.2.3. Universal adhesives

Universal adhesives can be applied either with the etch-and-rinse approach, self-etching approach, or selective enamel etching. The compositions of the universal adhesives are basically similar to the previous generation all-in-one adhesives with several improvements. The functional monomer in the universal adhesives is mainly 10-MDP, which is relatively more hydrophobic compared with other functional monomers [33,34]. Furthermore, the hydrophilic components are minimized, *e.g.*, the concentration of HEMA in Clearfil Tri-S Bond Plus and Clearfil Universal Bond Quick is 10–35% and 2.5–10%, respectively [35,36]. Finally, the pH of the universal adhesives ranges between 1.5–3.2; thus, most of them are classified as mild and ultra-mild self-etching adhesives [37]. Therefore, the adverse effect of the smear layer should be carefully concerned when the clinicians apply universal adhesives to dentin in the self-etching approach.

4. Smear layer characteristics

4.1. Instrument used for smear layer preparation

The smear characteristics depend on the armamentarium used. The two most common instruments used for dentin surface preparation in literature are SiC paper and burs. SiC paper is used only in laboratory research to standardize the smear layer and roughen the tooth substrate before performing the bond strength test. It has been recommended to use wet sanding to polish the surface with a circular motion [38]. In some studies, dental burs, such as a diamond bur or carbide bur, were used to produce a clinically relevant smear layer. Special equipment, *e.g.*, a CNC specimen former, was used to stabilize the handpiece during surface preparation [27]. However, free hand preparation of the smear layer using burs would be more clinically relevant. Fig. 2 demonstrates the smear layers resulting from different surface preparations.

Surface preparation using erbium-doped:yttrium-aluminium garnet (Er:YAG) laser has been reported to be more advantageous than preparation using burs [39]. Though the process is time-consuming, Er:YAG laser causes water micro-explosions, together with the vaporization and melting of organic and inorganic components. The prepared surface is then free of smear layer where the improved bond strength should be expected [40]. However, subsurface dentin fissuring [41] and the inferior bonding performance after laser ablation has been noted [42].

Airborne-particle abrasion is also used for caries removal [43,44], tooth preparation [45], and surface roughening [46]. The aluminum oxide particle is commonly used to prepare the surface. The rough surface is beneficial to the bonding performance of adhesive by increasing surface area for resin adhesion [47]. On the other hand, Ouchi et al. [48] reported that the dentin bond strength of universal adhesives in self-etching mode significantly decreased after the surface was grit-blasted with alumina particle. They suggested that such adverse effect was caused by the compaction of the smear layer after alumina grit-blasting, which might inhibit the adhesive resin penetration. However, according to the recent systematic review and meta-analysis, it has been concluded that the airborne-particle abrasion with alumina presented no adverse effect on the dentin bond strength [49]. They recommended using the particle size larger than 30 μm with an air pressure of more than 5 bar to improve the bond strength. For the clinical application, the splattering of the particles within the operating field is inevitable. The use of rubber dam isolation with high-velocity evacuation devices is mandatory [50]. In addition, the patients and dental personnel must also be equipped with protective eyewear to prevent accidental eye irritation.

4.2. Smear layer thickness

The smear layer thickness typically depends on the size of the abrasive particles used. The bigger the abrasive particle size is, the thicker smear layer will be formed [9,26,51]. Tani and Finger reported the thickness of the smear layer ranging from 0.9 to 2.6 μm for the SiC-ground smear layer and 1.0 to 2.8 μm for diamond bur-cut smear layer [51]. Oliveira et al. demonstrated that the thickness of the carbide bur-prepared smear layer was 1.8 μm, which was similar to those prepared by SiC papers and diamond burs, except for the 240-grit SiC paper where the 3.0-μm-thick smear layer was observed [9]. It might be difficult to compare the thickness of the smear layer from different instruments between literatures. However, when comparing between the most commonly used instruments (SiC paper and diamond burs) with corresponding abrasive particle sizes, the SiC-ground smear layers have been shown to be significantly thicker than those prepared by diamond burs [9,26].
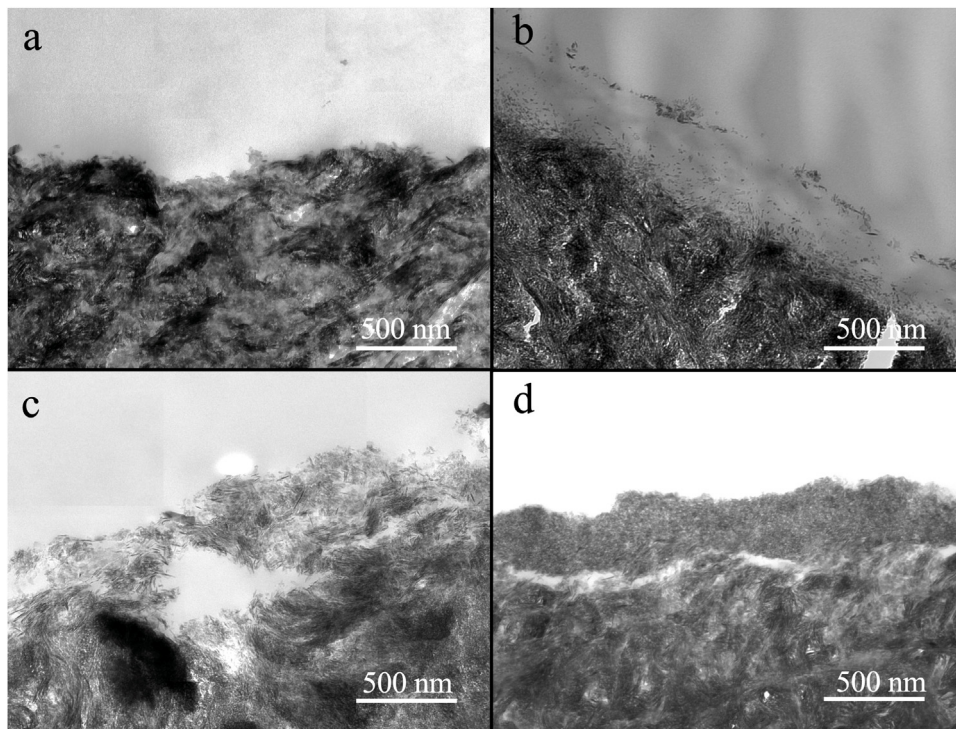
Fig. 2. Representative TEM images of dentin surfaces with different surface preparations. (a) No smear layer was detected in the fractured dentin specimen. (b) The smear layer prepared by a carbide bur was loosely bound to the dentin surface with approximately 300 nm-in-thickness. (c) The smear layer prepared by SiC paper was non-homogenous. (d) The smear layer prepared by a regular diamond bur was the most compact.

4.3. Smear layer density

The smear layer density or denseness is the degree of the smear compaction which is also influenced by the preparation instruments [9,27]. A dense smear layer was observed when prepared using diamond burs, whereas a loosely organized smear layer was detected when prepared using SiC paper [9,27,52]. Although both instruments are used with a similar abrade motion, the higher cutting speed of a diamond bur could compress the preparation debris into a more compact smear layer [9,10,27]. Mine et al. demonstrated that the ultra-mild self-etching adhesive could not completely demineralize and infiltrate to the diamond bur-cut smear layer [5]. In contrast, the smear layer produced by carbide burs is thin and loosely bound. This might be due to the different cutting motion of the carbide bur because a new surface is produced when the cutting blade scrapes the dentin surface [27].

The cutting speed also has influence on the smear layer density and bonding performance of self-etching adhesives. The fissure steel bur with low-speed cutting (2000 rpm) demonstrated similar smear layer characteristics when compared to those prepared by 600-grit SiC paper [53,54]. The etching patterns of self-etching primer on those surfaces were also similar. On the contrary, the coarse diamond bur with high-speed cutting (100,000–120,000 rpm) produced a thick smear layer, which was subsequently more difficult to be removed by self-etching primers [53,54].

The smear layer density was indirectly evaluated by counting the number of occluded dentinal tubules [9] and the reaction of the smear layer after applying acidic agents, *e.g.*, phosphoric acid or self-etching adhesives, using a scanning electron microscope (SEM) [27,55]. A recent study demonstrated the characteristics of the smear layer using transmission electron microscopy (TEM) in a longitudinal direction [10]. With this technique, the density and the reaction of the smear layer to various acidic agents can be evaluated directly, as presented in Fig. 3 [10,56].

The density of the smear layer is more critical than its thickness, especially for mild- and ultra-mild self-etching adhesives [5,10,26,29,31]. Acidic monomers are less effective in interacting with a dense smear layer for the dissolution. Therefore, resin penetration is hindered, resulting in low bond strength. In contrast, it is easier for mild acidic monomers to remove the loosely-organized SiC-ground smear layer and penetrate into the underlying dentin, forming a uniform hybrid layer and resin tags [50,57].

5. Application techniques to improve the bonding performance of self-etching adhesives

As mentioned above, most of the universal adhesives currently available are mild and ultra-mild self-etching adhesives. The weak acidity of these adhesives can be buffered by the smear layer, especially one created using a diamond bur [5,26,31,32]. Therefore, bonding modifications either with chemical agents or adhesive application techniques might be optional to improve the bonding performance of these adhesives.

5.1. Chemical agents

There are several chemical agents that can be used to modify the smear layer. The mechanisms of these agents depend on the compositions of the smear layer targeted. The organic components of the smear layer can be dissolved using deproteinizing agents [58,59], while the inorganic component can be bound using chelating agents [60,61].

Sodium hypochlorite (NaOCl) and hypochlorous acid (HOCl) are the recommended deproteinizing agents for modifying the smear layer [62–64]. The collagen fibrils in the smear layer can form hydrogen bonds with water. Consequently, the hydrated collagen fibrils inhibit resin penetration and polymerization. Therefore, it has been recommended to remove the collagen before applying the adhesive [65,66]. However, residual oxygen species can be gener-
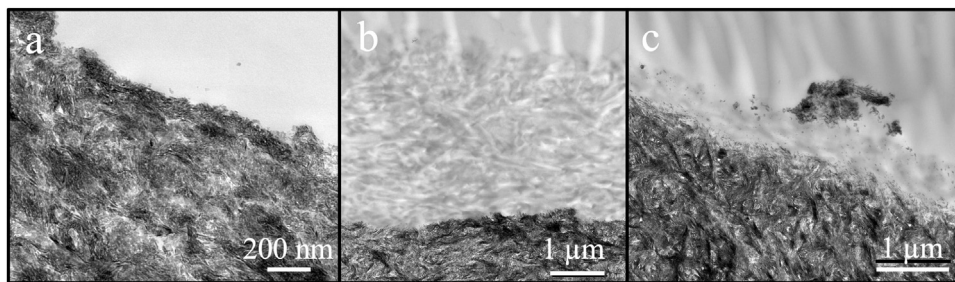
Fig. 3. TEM observation of dentin surface prepared by superfine diamond bur in longitudinal view (a). The dentin surface was etched with 35% phosphoric acid solution (b) and treated with Clearfil SE2 primer (Kuraray Noritake; Tokyo, Japan) (c).
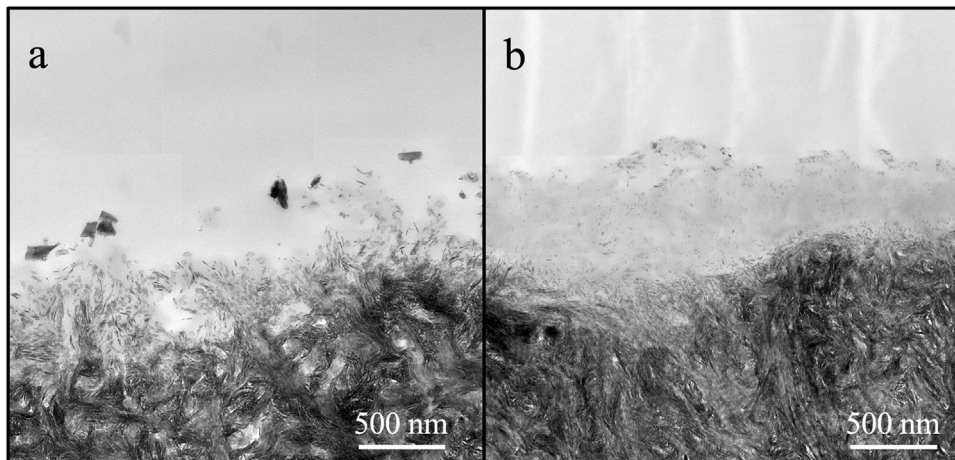

Fig. 4. Representative TEM images of superfine diamond bur-prepared smear layers treated with Clearfil SE2 primer (Kuraray Noritake; Tokyo, Japan) with the inactive application (a) or active application (b).

ated after irrigating with deproteinizing solutions [67]. The residual oxygen species also inhibit resin polymerization and affect the resin-dentin bond strength [67–69]. It is then suggested to reverse the bond strength of the deproteinized dentin by using antioxidants or reducing agents. Antioxidants scavenge the oxygen, and many of them can be used to reverse the bond strength of the deproteinized dentin. The effectiveness of antioxidants depends on the number of hydroxyl (−OH) groups in each molecule [70]. A previous study reported that the dentin bond strength of NaOCl-treated dentin could be reversed by irrigating with 10% ascorbic acid for 1 min [71]. Another investigation also demonstrated a promising effect of rosmarinic acid and p-toluenesulfinic acid sodium salt solution (Accel; Sun Medical, Kyoto, Japan) on deproteinized dentin by rinsing for 5 s prior to the adhesive application [72]. The combination of a deproteinizing agent and an antioxidant is currently the best option to dissolve the organic phase of the smear layer with no adverse effect on polymerization.

Ethylenediaminetetraacetic acid (EDTA) is used to selectively remove the inorganic component from the smear layer due to its ability to bind to hydroxyapatite [73]. The effect of EDTA depends on the concentration used and time of application [73–75], where the irrigation with 17% EDTA for 1 min has been recommended [76]. Partial removal of the smear layer without altering the morphology of the underlying dentin has been observed after using EDTA [77,78]. It has also been advised to pre-treat the dentin with EDTA instead of using phosphoric acid [73]. Although the chelating effect produced by EDTA was milder than the etching potential of phosphoric acid [79], the resistance to resin-dentin bond degradation was improved with EDTA conditioning [80,81]. However, the bond strengths of self-etching adhesives to EDTA-treated dentin are inconsistent. No benefit from EDTA has been observed when the smear layer was treated with 0.5 M EDTA (pH 7) for 2 min before

bonding with self-etching adhesives [82]. On the contrary, the bond strength of Clearfil SE Bond significantly increased after dentin conditioning with 0.5 M EDTA at pH 7.2 for 30 s [83]. Another study also demonstrated improved dentin bond strength with two self-etching adhesives after applying 24% EDTA gel (pH 7.0) for 1 min [84]. Nevertheless, these studies have evaluated the bond strength to SiC-ground dentin. Further investigations determining the effect of EDTA pretreatment on bur-cut dentin are needed.

5.2. Modified techniques of the adhesive application

The adhesive application can be modified mechanically to improve the smear layer removal. The suggested modified techniques are the active application and the multiple application of the adhesive.

Active application is to rub the adhesive with force on the tooth substrate during application. Using this method, the smear layer dissolution is enhanced by force applied and the stirring effect (Fig. 4) [85]. However, no significant difference in bond strength was detected when various forces were used [86]. There are also many benefits of active application technique in addition to the improvement of smear layer removal, such as promoting the chemical interaction with the 10-MDP monomer [87], enhancing the solvent evaporation [88], ameliorating the bond durability [89], increasing resin penetration and reducing nanoleakage [90].

Ultrasonic treatment is also used to remove the smear layer. Nakabayashi and Saimi removed the smear layer by polishing the dentin surface with hydroxyapatite paste and immersing it in an ultrasonic cleaner [91]. The technique was modified by Saikaew et al. to remove the smear layer with an ultrasonic cleaner followed by brushing with an ultra-soft toothbrush [26]. However, these techniques are not clinically relevant. Many studies have inves-
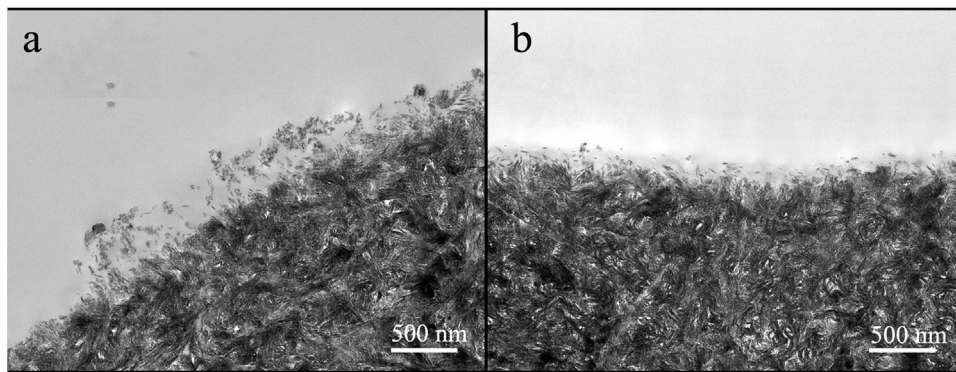
Fig. 5. Representative TEM images of superfine diamond bur-prepared dentin treated with Scotchbond Universal adhesive (3 M Oral Care; St. Paul, MN, USA) with single application (a) or double application (b).

tigated the modification of using an ultrasonic device to clinically remove the smear layer. One study attached a custom-made brush to the tip of an ultrasonic scaler to remove the smear layer prior to applying the adhesive. With this technique, the smear layer thickness decreased, and a higher bonding performance was achieved after ultrasonic brushing for 30 s [92]. An ultrasonic device was also used in another study to agitate the adhesive during application. The benefit of this technique was, however, material-dependent [93].

The adhesive application time has been indicated by the manufacturer to warrant the optimal bond strength. Basically, applying the adhesive at the time according to the manufacturer's instructions is a minimum requirement to ensure the sufficient interaction between resin monomer and underlying dentin [94–96]. Notably, some manufacturers claimed that their universal adhesives, *i.e.,* G-Premio Bond and Clearfil Universal Bond Quick, can be applied using less time without compromising the bond strength [97,98]. It has been demonstrated that less application time resulted in inferior bonding performances [94–96,99]. However, in several studies, applying the universal adhesives with less time demonstrated a stable bond after 1 year [95] and 2 years of water storage [100].

Increasing the adhesive application time is also recommended to improve the bond strength. A significant effect was found after extending the application time to 90 s and 150 s for acetone-based and ethanol-based adhesive, respectively [101]. The results from another study, however, demonstrated no significant effect from doubling the application time [102]. A plausible explanation might be that the prolonged application time increases solvent evaporation rather than enhances the smear layer dissolution.

Multiple adhesive application has been proposed by Frankenberger et al. to ensure that the entire dentin surface is coated with the adhesive [103]. A study demonstrated the benefits of applying the adhesive twice, both with and without light-curing between each coat [104]. These two techniques demonstrated significantly higher bond strength compared with a single application. However, the mechanisms for the improvement of bonding performance are different. By applying the adhesive twice without light-curing between each coat, the smear layer dissolution is enhanced due to the higher concentration of the acidic monomer (Fig. 5). This technique also allows more time for demineralization and interaction to the underlying dentin with the resin monomers. Thus, the smear layer removal and the resin penetration can be improved [56,104]. In contrast, the improved bonding performance after double application with light-curing between each coat is mainly due to the thicker adhesive layer and better mechanical properties of the resin-dentin interface, rather than enhancing the smear layer interaction.

6. Conclusion

The smear layer characteristics differently affect the bonding performances of self-etching adhesives. As most of the so-called universal adhesives can be classified as mild- and ultra-mild self-etching adhesives, the bonding performances can also be influenced by the smear layer when applied in self-etching approach. Their adhesion potential can be improved by enhancing the smear layer removal, both chemically and mechanically. Chemical agents such as NaOCl or EDTA, can be used prior to the adhesive application to interact with the organic component and inorganic component of the smear layer, respectively. Whereas, mechanical smear layer removal can also be improved by modifying the adhesive application. From this review article, we recommend the clinicians to use the adhesive according to the manufacturer's recommended application time with active application and/or double adhesive application. We urge that future investigations should focus on the long-term results when bonded to a clinically relevant smear layer.

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Conflict of interest

The author confirms that there is no conflict of interest to be declared.

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