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Review Article

Bonding to caries-affected dentin

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Summary Dentin adhesive systems have dramatically developed during the past decades. In a prepared cavity for an adhesive composite restoration, large areas of the cavity floor are composed of caries-affected dentin after removal of caries-infected dentin, not normal dentin. Caries-affected dentin is different in morphological, chemical and physical characteristics from normal dentin. Therefore, caries-affected dentin has still problems as bonding substrate compared with normal dentin. That is, caries-affected dentin produces lower bond strength and poor quality of the hybrid layer than normal dentin. In addition, when exposed the adhesive interface of caries-affected dentin in oral environment, the poor quality of the hybrid layer would compromise the longevity of the composite restoration due to hydrolysis of the resin and collagen fibrils. The improvement of bonding potential to caries-affected dentin could lead to reinforcement of tooth-composite restoration complex, protecting secondary caries and tooth fracture.

Contents

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Introduction

Dental caries is the most common pathological change of dentin. Fusayama's research demonstrated that carious dentin consists of two distinct layers: an outer layer of bacterially infected dentin, and an inner layer of affected dentin [1]. The outer layer (caries-infected dentin) was characterized as being highly demineralized, physiologically unremineralizable and showing irreversible denatured collagen fibrils with a virtual disappearance of cross-linkages. The inner layer (caries-affected dentin) is uninfected, partially demineralized and physiologically remineralizable, therefore should be preserved during clinical treatment. Consequently, in cavity preparation for an adhesive restoration after removal of caries-infected dentin, large areas of the cavity floor are composed of caries-affected dentin. Therefore, in clinical settings, bonding substrate is commonly caries-affected dentin, not normal dentin.

Many studies on dentin bonding have used normal dentin as bonding substrate, which have contributed to the dramatic development of dentin adhesive systems during the past decades. On the other hand, there is a few study about bonding to caries-affected dentin, in which the bond strengths to caries-affected dentin are lower than those of normal dentin [2–13] (Table 1). The inferior bonding efficacy of caries-affected dentin would affect the clinical performance of adhesive composite restoration. This article discusses bonding potential to caries-affected dentin and also reviews the characteristics of caries-affected dentin.

Characteristics of caries-affected dentin

Mineral phase

The mineral phase of dentin is mainly composed of carbonate-rich hydroxyapatite. The dentinal caries process consists of dynamic, cyclical episodes of demineralization and remineralization. A Fourier-transform infrared imaging (FTIR) study has shown that the mineral phase of caries-affected dentin is less crystalline and has a lower mineral content than normal dentin [14]. Micro-Raman spectroscopy investigation has suggested that the relative intensity of the mineral carbonate peak at $1070\,\text{cm}^{-1}$ decreased dramatically in caries-affected dentin [15]. Electron probe microanalysis (EPMA) revealed that caries-affected dentin, as well as caries-infected dentin showed much lower magnesium (Mg) content compared with intact dentin, although the densities of calcium (Ca) and phosphorus (P) in caries-affected dentin were relatively similar to intact dentin [8] (Fig. 1). The reduction in Mg content in dentin starts before the commencement of a decrease in Ca and P content in dentinal caries [16,17]. Changes in Mg content could be the first sign of carious demineralization and may indicate a loss of peritubular dentin matrix [18]. Moreover, larger apatite crystals are present in remineralized dentin after carious demineralization, compared to the apatite crystals in intact dentin [17,19]. These indicate that caries-affected dentin causes re-precipitation of CO_3- and Mg-poor apatite after the dissolution of CO_3- and Mg-rich apatite [20,21]. Mineral crystals in caries-affected dentin are scattered and randomly distributed, with larger apatite crystallites and wider intercrystalline spaces compared with intact dentin [19].

Organic phase

The dentin organic matrix contains different extracellular proteins, such as type I collagen, proteoglycans, dentin phosphoproteins and sialoprotein. Changes in dentin organic matrix associated with caries have been reported [15,22–24]. In the inner layer (caries-affected dentin), the general pattern of amino acid composition shows no significant differences from intact dentin [22]. In addition, the reducible intermolecular covalent cross-links of the collagen are partly shifted to the precursor form, thus leading to decreased cross-links—but this change is reversible [22], and the 67-nm cross-bands of the collagen fibrils remain [23]. These results support the idea that caries-affected dentin is remineralizable. On the other hand, the secondary structure of collagen is slightly altered by the carious process [15], and the distribution of antigenically intact collagen fibrils and proteoglycans is significantly lower in normal dentin [24]. Reductions in antigenicity from the organic matrix of sclerotic dentin under caries lesions raise concern about the potential of interfibirillar remineralization [24].

Transparent layer

Under a caries process, continuous deposition of minerals occurs within the tubule lumen (Fig. 2). In fact, most of the dentinal tubules in caries-affected dentin are occluded by mineral crystals [25]. The crystals in the tubule lumen render the refractive index of the lumen similar to that of the intertubular dentin, making the transparent layer. In these mineral deposits, Mg was identified although Mg was barely present in intertubular caries-affected dentin [9]. Therefore, intratubular minerals consist of large rhombohedral crystals of Mg-substituted β-TCP (whitlokite) [26], which is less soluble than hydroxyapatite.

Water content and permeability

As mineral is lost from the dentin matrix during the carious process, its volume is replaced by water. The water content of normal dentin is approximately 10%, whereas that of caries-affected dentin shows a higher value, which varies from 14% to 53% [27]. On the other hand, permeability of caries-affected dentin decreases due to occlusion of the tubules. Tagami et al. [28] found young carious molars were

Table 1 The review papers concerning about bond strength to caries-affected dentin.

Author	Ref.	Adhesive material	Manufacturer	Bonding system	Bonding procedure	Test method	Normal dentin		Caries-affected
Nakajima et al. (1995)	[2]	All Bond 2	Bisco	Etch and rinse(wet)	3-Step	μTB(hourglass)	26.90	$p < 0.05$	13.01
		Scotchbond Multi-Purpose	3 M	Etch and rinse(dry)	3-Step		20.32	NS	18.49
		Clearfil Liner Bond 2	Kuraray	Self-etch	2-Step		29.52	$p < 0.05$	13.97
Nakajjima et al. (1999)	[3]	Scotchbond Multi-Purpose	3 M	Etch and rinse(wet)	3-Step	μTB(hourglass)	42.4	NS	48.2
Nakajjima et al. (1999)	[4]	Clearfil Liner Bond 2	Kuraray	Self-etch	2-Step	μTB(hourglass)	45.2	$p < 0.05$	29.7
		Clearfil Liner Bond 2V	Kuraray	Self-etch	2-Step		57.4	$p < 0.05$	39.1
		ART Bond	Coltene	Self-etch	2-Step		24.9	NS	30.2
Yoshiyama et al. (2000)	[5]	FluoroBond	Shofu	Self-etch	2-Step	μTB(hourglass)	28.2	$p < 0.05$	17.5
		Single Bond	3 M ESPE	Etch and rinse(wet)	2-Step		46.0	$p < 0.05$	27.1
		Single Bond		Etch and rinse(dry)	2-Step		26.4	$p < 0.05$	18.1
Yoshiyama et al. (2002)	[6]	ABF (Clearfil Protect Bond)	Kuraray	Self-etch	2-Step	μTB(dumbbell)	44.9	$p < 0.05$	25.3
		Single Bond	3 M ESPE	Etch and rinse	2-Step		50.9	$p < 0.05$	28.8
Ceballos et al. (2003)	[7]	Prime and bond NT	Dentsply	Etch and rinse	2-Step	μTB(hourglass)	56.3	$p < 0.05$	41.3
		Scotchbond 1	3 M ESPE	Etch and rinse	2-Step		43.9	NS	36.3
		Clearfil SE Bond	Kuraray	Self-etch	2-Step		35.5	$p < 0.05$	21.5
		Adper Prompt L Pop	3 M ESPE	Self-etch	1-Step		18.2	NS	13.4
Doi et al. (2004)	[8]	Clearfil SE Bond	Kuraray	Self-etch	2-Step	μTB(hourglass)	41.2	$p < 0.05$	21.5
		Mac-Bond II	Tokuyama	Self-etch	2-Step		35.0	$p < 0.05$	20.2
		Unifil Bond	GC	Self-etch	2-Step		27.2	$p < 0.05$	19.6
Nakajima et al. (2005)	[9]]	Clearfil Protect Bond	Kuraray	Self-etch	2-Step	μTB(hourglass)	43.5	$p < 0.05$	29.4
Say et al. (2005)	[10]	Optibond Solo Plus Total-etch (photo-cure)	Kerr	Etch and rinse	2-Step	μTB(hourglass)	38.7	$p < 0.05$	28.5
		Optibond Solo Plus Self-etch (photo-cure)		Self-etch	2-Step		44.2	$p < 0.05$	29.2
		Optibond Solo Plus Total-etch (dual-cure)		Etch and rinse	2-Step		17.2	$p < 0.05$	10.5
		Optibond Solo Plus Self-etch (dual-cure)		Self-etch	2-Step		18.3	$p < 0.05$	13.5
Pereira et al. (2006)	[11]	Single Bond	3 M ESPE	Etch and rinse	2-Step	μTB(hourglass)	43.3	NS	36.1
		Adper Prompt L Pop	3 M ESPE	Self-etch	1-Step		52.0	$p < 0.05$	37.3
Wei et al. (2008)	[12]	Clearfil SE Bond	Kuraray	Self-etch	2-Step	μSB	44.96	$p < 0.05$	33.76
		Clearfil Tri-S Bond	Kuraray	Self-etch	1-Step		40.48	$p < 0.05$	33.3
		Single Bond	3 M ESPE	Etch and rinse	2-Step		44.69	$p < 0.05$	32.65
Scholt anus et al. (2010)	[13]	Scotchbond 1XT	3 M ESPE	Etch and rinse	2-Step	μTB(bar)	35	$p < 0.05$	25
		Clearfil Tri-S Bond	Kuraray	Self-etch	1-Step		35	$p < 0.05$	21
		Clearfil SE Bond	Kuraray	Self-etch	2-Step		33	NS	39

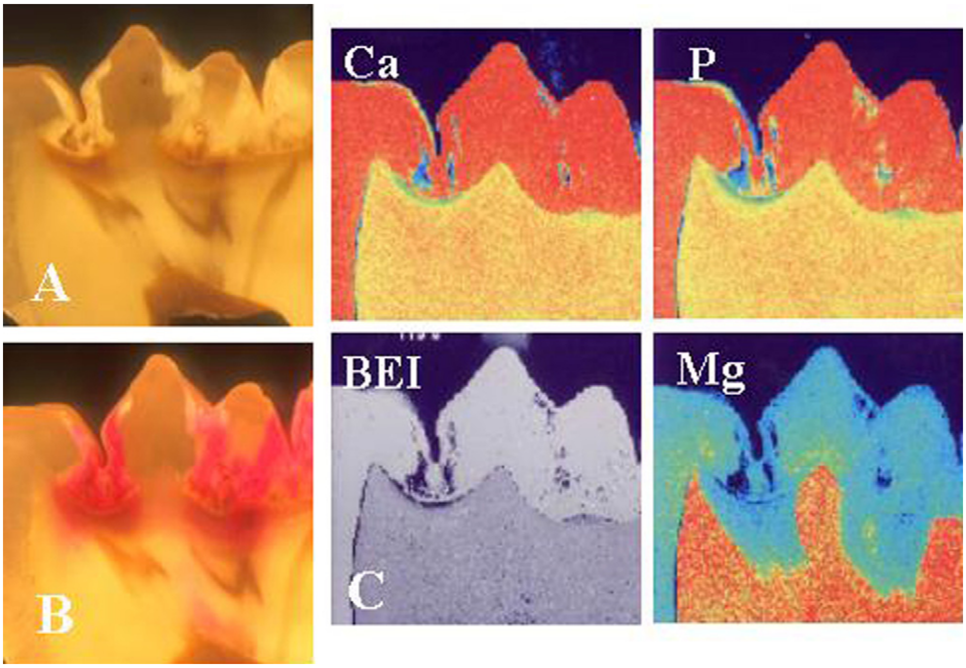

Figure 1 Light microscopic photographs and EPMA mapping images of carious tooth [9]. (A) Cross-sectioned specimen of carious tooth; (B) specimen A stained by caries detector solution; (C) mapping images of elemental distribution (Ca, P, Mg) and backscatter electronic image of specimen A observed by EPMA. Mg-depleted area corresponds well to the morphological changes seen in light microscope images (A and B).

only 14% as permeable as young normal dentin and suggested that the transparent layer would be effective in decreasing permeability.

Mechanical properties

Caries-affected dentin is softer than normal dentin, with about half the hardness, even though mineral depositions occlude dentinal tubules [2,7,11,25,29—31]. In addition, ultimate tensile strength (UTS) of caries-affected dentin is also lower than that of normal dentin, and there is a positive correlation in caries-affected dentin between the UTS and the Knoop hardness number [6]. On the other hand, Nishitani et al. [32] reported that the matrix of demineralized caries-affected dentin was as strong as that of normal demineralized dentin. These results would indicate that lower UTS and hardness of caries-affected dentin are due to loss of mineral in intertubular dentin. Marshall et al. [29] reported that the mean elastic modulus (18.2 GPa) and nanohardness (0.8 GPa) of intertubular dentin on the transparent layer were slightly, but significantly lower than those of the unaffected intertubular dentin (20.6 and 1.0 GPa, respectively). On the other hand, for arrested caries, the elastic modulus of the transparent layer of caries-affected dentin is not significantly different from the underlying normal dentin although its hardness is lower than normal dentin [30,31].

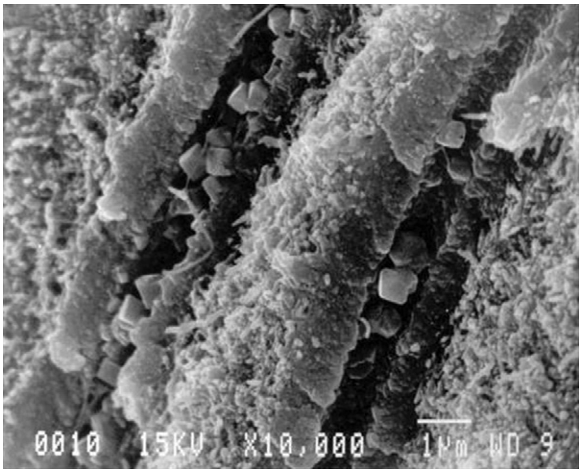

Figure 2 Scanning electron micrograph (SEM) of the transparent layer of caries-affected dentin [28]. Many mineral casts occludes dentinal tubules.

Smear layer

Cavity preparation with rotary instruments or others results in the formation of a smear layer on the dentin surface, in which the cutting method affects smear layer characteristics (i.e. thickness, density). The smear layer fills the orifices of dentinal tubules, to form smear plugs, leading to a reduction in dentin permeability. However, sub-micron porosities in the smear layer still allow for the diffusion of dentinal fluid. The dentin smear layer with smear plugs is composed mostly of submicron particles of mineralized collagen debris [33,34], which differs little in composition from the underlying dentin [33—35]. Therefore, the smear layer formed on caries-affected dentin would be different in morphological and chemical structures from that of normal dentin, because caries-affected dentin is partially demineralized, leading to different mineral/organic contents compared to normal dentin. Indeed, the smear layer of caries-affected dentin is

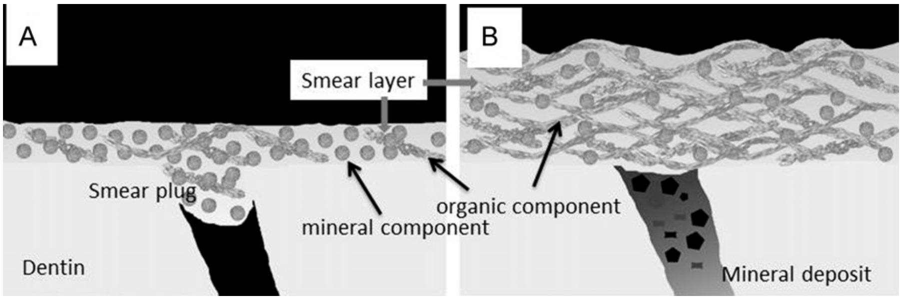

Figure 3 Schematic illustration of smear layers of normal and caries-affected dentin. Caries-affected dentin smear layer is thick with enriched organic components compared with normal dentin smear layer.

thicker and appears to be enriched with organic components compared with that of normal dentin (Fig. 3) [36,37].

Bonding to caries-affected dentin

Caries-affected dentin produces lower bond strengths than normal dentin, regardless of the type of adhesive system (etch and rinse system or self-etch system; one-, two- or three-step of bonding procedure) [2—13,36—39], in which cohesive failure of specimens in dentin increases in resin-bonded caries-affected dentin [6,7,10]. A reduction in the cohesive strength of caries-affected dentin would be one of the reasons for lower bond strength values to caries-affected dentin compared with normal dentin [6]. On the other hand, Wei et al. [12] demonstrated that when analyzing the effect of dentin type (normal and caries-affected dentin) on bond strength after removing the variance for which hardness accounted as a covariate, it was found that the condition of dentin had a significant effect on bond strength: even if normal and caries-affected dentin had similar intertubular hardness, bond strength to caries-affected dentin would still be significantly lower than to normal dentin. The change in chemical and morphological characteristics of caries-affected dentin would be also reasons for the lower bond strength. The hybrid layers created to caries-affected dentin are thicker than those of normal dentin, because caries-affected dentin is more susceptible to the acid etching due to partially demineralization, resulting in the formation of a deeper demineralized zone [2—6,8—10,15,38,40].

Etch and rinse adhesive system

When phosphoric acid etchants are applied to normal and caries-affected dentin surface, the smear layer is completely removed, and both dentinal sub-surfaces are demineralized and the collagen fibrils are exposed. In order to produce a superior resin—dentin interface, resin monomers must penetrate into these demineralized dentinal sub-surfaces. However, even though for normal dentin, it has been demonstrated that there are discrepancies between the depths of demineralization and resin monomer penetration. The wet bonding technique is effective for infiltration of resin monomers into deeper acid-etched demineralized layers in caries-affected dentin compared with the dry bonding technique, leading to higher bond strength [4,5]. Nevertheless, a deeper demineralized zone is more difficult for resin monomer to penetrate to the bottom of the exposed collagen matrix. In addition, a larger quantity of water in the deeper demineralized zone would compete with penetration of the adhesive resin monomers. Besides the residual water, caries-affected dentin may contain substances that interfere with free radical generation or propagation, leading to poor polymerization of adhesive monomers. It is reported that the degree of conversion of adhesive agent that penetrated the etched dentin in the caries-affected dentin specimen was lower than in the normal dentin specimens [14].

The mineral deposits in dentinal tubules in the transparent layer are highly acid resistance. Etching with phosphoric acid cannot completely dissolve the deposits that exist in dentinal tubules without dissolution. The presence of mineral deposits inside dentinal tubules would interfere with resin monomer infiltration peripheral to the dentinal tubules as well as resin tag formation, leading to lower bond strength [2,5].

The hybrid layer of etch and rinse system in caries-affected dentin was thicker but susceptible to the acid and base treatment in scanning electron microscopy (SEM) observation of resin/caries-affected dentin interface [2] (Fig. 4). Transmission electron microscopy (TEM) observation demonstrated a more porous zone along the base of the hybrid layer in caries-affected dentin created [6]. Micro-Raman spectroscopy investigation suggested that the caries-affected dentin interface was more complicated, whereby the wider demineralized matrix was not protected by the critical Bis-GMA [15]. Light microscopy evaluation with Masson's trichrome stain indicated wider regions of non-encapsulated collagen in the caries-affected dentin interface [40]. These would be due to reduced penetration of the resin monomers into the etched caries-affected dentin because of the deeper demineralized zone and the presence of the mineral deposits inside the dentinal tubules (Fig. 5).

Etching with phosphoric acid might be too aggressive for partially demineralized intertubular caries-affected dentin. However, stronger acids and an extended etching time are suggested for solubilizing acid resistant mineral deposits within the caries-affected tubule lumens, leading to more lateral penetration of the adhesive monomer from the tubule lumens. When One-Step (Bisco) with 10% phosphoric acid etchant was applied to caries-affected dentin, it resulted in lower bond strength than normal dentin, however this significant difference disappeared following the application of 32% phosphoric acid [38]. Arrais et al. [39] reported that extending the etching time for 35% phosphoric acid from 15 s to 45 s duration improved the bond strength of Single Bond (3M ESPE) to caries-affected dentin. However, its bond

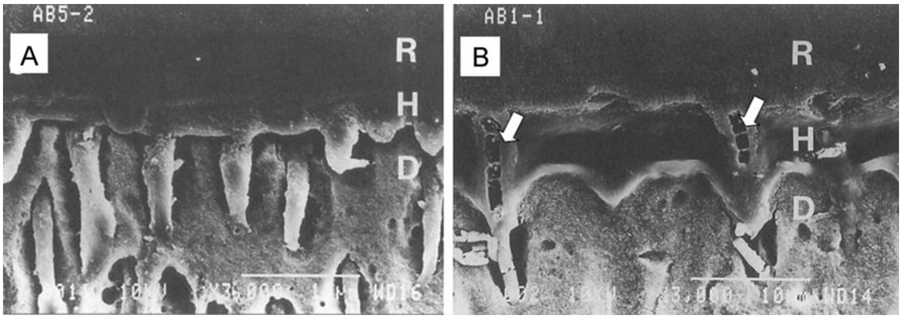

Figure 4 Scanning electron micrographs (SEM) of dentin specimens bonded with all bond 2 after acid and base challenge [2]. (A) Normal dentin: the hybrid layer is about 3—4 μm thick and was resistant to acid/base challenge; (B) caries-affected dentin: the hybrid layer is 5—7 μm thick The middle of the hybrid layer was partially removed by acid/base challenge. Tube-like structures of the resin tags would indicate presence of residual mineral casts before acid/base challenge. R = resin; H = hybrid layer; D = dentin.

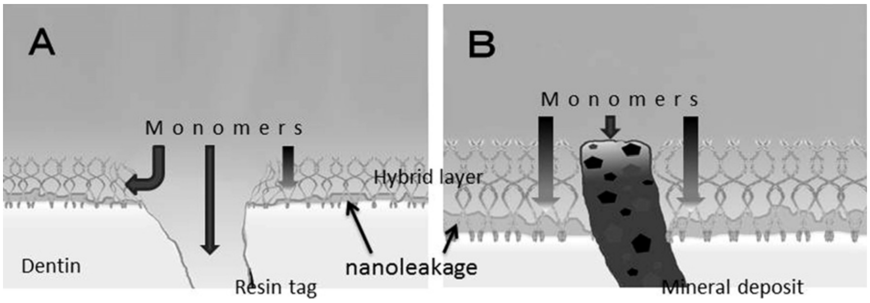

Figure 5 Schematic illustration of interface of normal and caries-affected dentin using etch and rinse adhesive. The mineral deposits in dentinal tubules interfere with resin monomer infiltration peripheral to the dentinal tubules as well as resin tag formation. Caries-affected dentin produces thicker hybrid layer, in which there are poorer infiltrations of resin monomers into etched dentin because of the deeper demineralized zone and the presence of the mineral deposits inside the dentinal tubules.

strength was still lower than that of normal dentin. Since a longer etching time would deepen the zone of demineralized intertubular dentin, the discrepancy between the demineralized layer and resin monomer penetration could not be eliminated.

Recently, the application of chemical cross-linker in the bonding procedures has been introduced, which may potentially increase dentin collagen stability due to a higher number of collagen cross-linkages [41]. When etch and rinse systems (One-step Plus, Bisco; Single Bond Plus, 3M ESPE) were used, application with the chemical cross-linking agents (glutaraldehyde and grape seed extract) for 1 h after acid etching significantly improved bond strength to caries-affected and sound dentin, in which the cross-linked dentin matrix might mechanically strengthen incomplete resin-infiltrated demineralized zone at the bottom of the hybrid layer [41].

Self-etch adhesive system

Self-etch systems have also exhibited lower bond strengths to caries-affected dentin than normal dentin, and their hybrid layers in caries-affected dentin are also thicker than those of normal dentin but absolutely thinner than those of etch and rinse systems [2,6,10,40]. Using self-etch adhesives, it has been generally accepted that there are fewer discrepancies between depths of demineralized zone and resin monomer penetration, because demineralization and resin monomer penetration occur simultaneously. However, TEM observation revealed a porous zone beneath the hybrid layer of self-etch system in caries-affected dentin [6]. Nakajima et al. [9] reported that there was a thicker nitrogen-rich layer at the caries-affected dentin interface of 2-step self-etch system using EPMA analysis, which is indicative of a collagen-rich phase (Fig. 6). Light microscopy evaluation with Masson's trichrome stain indicated wider regions of non-encapsulated collagen in the caries-affected dentin interface of 1-step and 2-step self-etch systems [40]. These results indicate that self-etch adhesives could not fully infiltrate adhesive monomers into the demineralized zone in caries-affected dentin.

Self-etch system cannot dissolve and remove acid-resistant mineral deposits in dentinal tubules of caries-affected dentin because of their higher pH. Therefore, an etch and rinse adhesive system using 30—35% phosphoric acid with stronger acidity might have the upper hand compared with self-etch systems, although phosphoric acid etching could not completely dissolve the mineral deposits in dentinal tubules in caries-affected dentin. However, using the same bonding agent of Optibond Solo Plus (Kerr), a total-etch technique with phosphoric acid did not have any beneficial effect on caries-affected dentin compared with the self-etch technique [10]. Even though for normal dentin, the mild acidity of self-etch systems is not sufficiently effective in the dissolution of smear plugs, therefore smear plugs are retained in the dentinal tubules as part of the hybridized complex with less resin tag formation. In this situation,

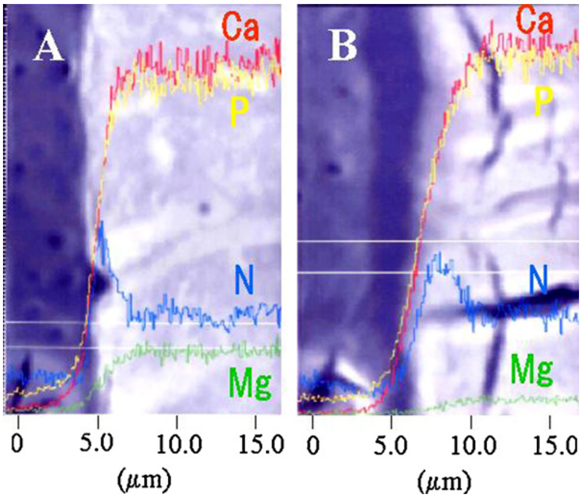

Figure 6 EPMA line analysis of Ca, P, Mg, and N at the adhesive interface of Clearfil Protect Bond [9]. (a) Normal dentin; (b) caries-affected dentin. N peaks were observed in the demineralized zones in both interfaces. An increase in N content occurred from the interface, peaked then decreased to a level similar to that of the underlying dentin. Demineralized zones in normal dentin and caries-affected dentin were 3.5 and 7 μm thick, respectively. D = dentin; A = adhesive resin; T = dentinal tubule. The line analysis was performed in two white line.

lateral penetration of the adhesive monomers from the dentinal tubules could not contribute to hybrid layer formation of self-etch adhesives. Therefore, for self-etch systems, the presence of mineral deposits in dentinal tubules would not be an important reason why caries-affected dentin causes less penetration of adhesive monomers, leading to lower bond strength than normal dentin, but a deeper mineralized zone would be the main reason. On the other hand, in the case of self-etch systems, the dentin smear layer would affect penetration of the adhesive monomers into the underlying dentin.

Several studies using normal dentin have demonstrated that dentin smear layer characteristics have been reported to compromise the bonding efficacy of self-etch systems. The smear layer on dentin is composed of disorganized collagen debris binding submicron mineral particles [33,34]. The smear layer of caries-affected dentin is thick and irregular, and appears to be enriched with organic components compared with that of normal dentin [36,37]. The disorganized collagen and/or the mineral trapped within the gelatinized collagen cannot be easily removed even when etched with phosphoric acid [43]. The disorganized collagen and the gelatinous layer within the smear layer may hinder resin monomer infiltration and prevent a perfect seal at the resin—dentin interface [34,43]. Therefore, the caries-affected dentin smear layer enriched with organic components would contribute to the inferior adhesion of self-etch adhesives to caries-affected dentin (Fig. 7).

Sodium hypochlorite solution (NaOCl) can effectively dissolve organic substrates from biological materials. Taniguchi et al. [36] demonstrated that NaOCl treatment of smear layer-covered caries-affected dentin eroded and thinned the smear layer due to dissolution of superficial organic components of smear layer (Fig. 8). Furthermore, they reported that pretreatment with 6% NaOCl for 15 s could significantly improve the bond strengths of 1-step and 2-step self-etch system to caries-affected dentin, while NaOCl-30 s pretreatment did not affect them [36]. On the other hand, for normal dentin, NaOCl-15 s pretreatment did not alter the bond strengths, but NaOCl-30 s pretreatment reduced them [36]. It has been speculated that applying NaOCl for 30 s or longer results in reactive residual free-radicals being present on the NaOCl-treated dentin that have been produced by the oxidizing effect of NaOCl and these compete with the propagation of vinyl free-radicals generated during light activation, resulting in premature chain termination and incomplete polymerization [44]. Applying a reducing agent (Accel; p-Toluenesulfinic acid sodium salt: Sun Medical) is effective in recovering the negative effect of NaOCl-oxidized dentin for 30 s on polymerization, leading to increased bond strengths to normal and caries-affected dentin [36]. Kunawarote et al. [37] reported the application of a mild acidic HOCl solution (Comfosy: Haccpper Advantec) as a pretreatment agent instead of NaOCl solution. Mild acidic HOCl solution is an antiseptic and an irrigant, which has outstanding properties because not only does it exhibit biocompatibility and low cytotoxicity but also has immediate and highly effective antimicrobial and deproteinizing properties. The 5 s pretreatment with 50 ppm Comfosy significantly improved the bond strengths of 2-step self-etch system to caries-affected dentin, but the 5 s pretreatment with 6% NaOCl did not affect them [37]. Pretreatment with mild acidic HOCl solution could be able to improve the quality of the hybrid layer of caries-affected dentin created by self-etching adhesives due to removal of disorganized/gelatinized collagen

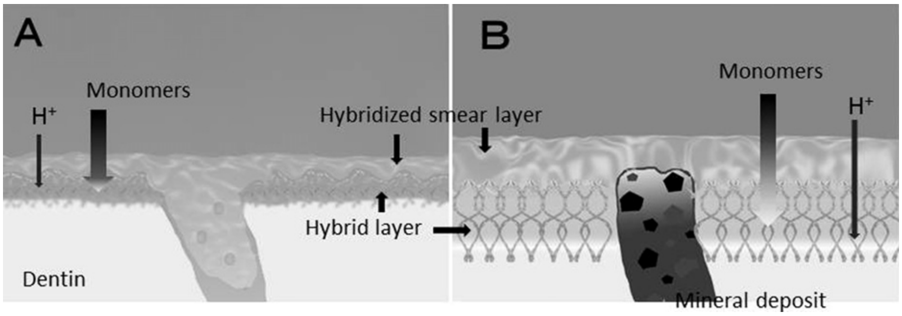

Figure 7 Schematic illustration of interface of normal and caries-affected dentin using self-etch adhesive. The gelatinized collagen in smear layer is not completely removed, forming hybridized smear layer. The thick gelatinous layer of caries-affected dentin smear layer would hinder resin monomer infiltration into underlying demineralized zone, resulting in poorer quality of the hybrid layer.

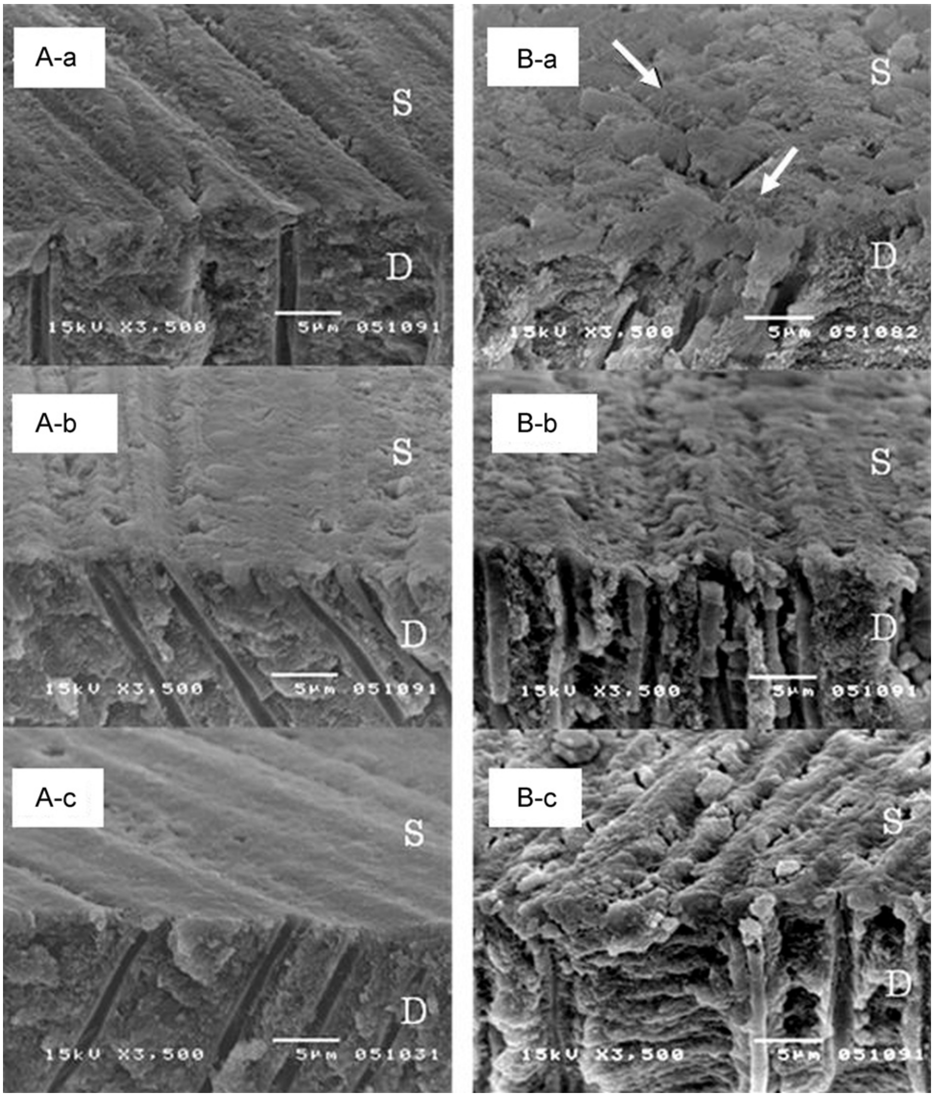

Figure 8 Scanning electron micrographs (SEM) of the #600 SiC-paper ground normal (A) and caries-affected dentin (B) surfaces [36]. (a) No treatment; (b) treated with 6% NaOCl for 15 s; (c) treated with 6% NaOCl for 30 s. For normal dentin, smear layer was smooth and compact. There were no significant alterations in surface morphological form. For caries-affected dentin, dentin surface was covered with a thick and irregular smear layer with sludge-like formation in which fibril-like structures were seen. After treatment with NaOCl, the smear layer was eroded and thinned in which fibril-like structures were not seen.

and enhancement of resin monomer penetration (Figs. 9 and 10), leading to more stable bonding to caries-affected dentin in long term (Table 2).

Bonding durability to caries-affected dentin

Adhesive restorations are exposed to a severe environment in the oral cavity. Occlusal stress, thermal stress and chemical attack by acid and enzymes affect the adhesive interface, compromising the integrity of adhesive restoration. A known degradation factor of resin—dentin bond is exposure to water. The exposed, altered collagen fibrils at the resin—dentin interface would be susceptible to further collagen disorganization or denaturation in the direct water exposure, leading to degradation of the bonded interface. Durability studies on bonding to caries-affected dentin are still limited [40,45—47] (Table 3). Erhardt et al. [40] reported that caries-affected dentin reduced the bond strengths regardless of the adhesive systems after direct exposure of the interface to water for 6 months. They indicated that the bonded interfaces of caries-affected dentin are more prone to hydrolytic degradation than those of normal dentin. Recently, Pashley et al. [48], demonstrated that host-derived matrix metalloproteinases (MMPs) enzymes in the dentin matrix promote the degradation of exposed, unprotected collagen within incompletely resin-infiltrated acid-etched dentin. The use of MMP inhibitor such as chlorhexidine, after acid etching, could prevent and minimize the degradation of exposed collagen within incompletely resin-infiltrated hybrid layers, contributing to the long-term stability of the hybrid layer and bond strength. Komori et al. [45] reported that chlorhexidine treatment for 60 s after acid etching significantly lowered loss of bond strengths of etch and rinse systems to normal

Table 2 The review paper concerning about improvement effect on bonding to caries-affected dentin.

Author	Ref.	Adhesive material	Manufacturer	Bonding system		Bonding procedure		Test method	Normal dentin		Caries-affected
Nakajima et al. (2000)	[38]	One-step	Bisco	Etch and rinse		32% H_3PO_4	Bond	μTB(hourglass)	49.7	NS	45.2
						10% H_3PO_4	Bond		47.7	$p < 0.05$	36.9
		Single Bond	3 M ESPE	Etch and rinse		35% H_3PO_4	Bond		49.5	$p < 0.05$	40.2
						10% H_3PO_4	Bond		51.7	$p < 0.05$	41.2
Arrrais et al. (2004)	[39]	Clearfil SE Bond	Kuraray	Self-etch		Self-etching primer	Bond	μTB(hourglass)	41.82	$p < 0.05$	23.06
						H_3PO_4 etching + self-etching primer	Bond		48.70	$p < 0.05$	30.76
		Single Bond	3 M ESPE	Etch and rinse		H_3PO_4	Bond		50.69	$p < 0.05$	23.58
						Extending H_3PO_4 etching for 45 s	Bond		43.74	$p < 0.05$	33.97
Erhardt et al. (2008)	[42]	Scotchbond 1	3 M ESPE	Etch and rinse		H_3PO_4	Bond	μTB(hourglass)	31.9	$p < 0.05$	26.2
						EDTA	Bond		28.1	NS	24.9
						H_3PO_4 + chlorhexidine	Bond		27.3	NS	23.8
Taniguchi et al. (2009)	[36]	Clearfil Protect Bond	Kuraray	Self-etch		Self-etching primer	Bond	μTB(hourglass)	40.9	$p < 0.05$	27.9
					NaOCl (15 s)	Self-etching primer	Bond		42.0	NS	41.6
					NaOCl (30 s)	Self-etching primer	Bond		34.3	NS	33.3
					NaOCl (30 s) + accel	Self-etching primer	Bond		37.5	NS	39.9
		Bond Force	Tokuyama	Self-etch			Bond		44.0	$p < 0.05$	29.8
					NaOCl (15 s)		Bond		43.7	NS	40.6
					NaOCl (30 s)		Bond		30.4	NS	31.4
					NaOCl (30 s) + accel		Bond		36.8	NS	35.6
Macedo et al. (2009)	[41]	Single Bond Plus	3 M ESPE	Etch and rinse		H_3PO_4	Bond	μTB(beam)	59.62	$p < 0.05$	36.75
						H_3PO_4 + glutaraldehyde	Bond		71.89	$p < 0.05$	55.55
						H_3PO_4 + grape seed extract	Bond		68.34	$p < 0.05$	55.9
		One-Step Plus	Bisco	Etch and rinse		H_3PO_4	Bond		65.22	$p < 0.05$	37.38
						H_3PO_4 + glutaraldehyde	Bond		74.30	$p < 0.05$	57.18

						H_3PO_4 + grape seed extract	Bond		73.14	$p < 0.05$	52.85
Kunawarote et al. (2011)	[37]	Clearfil SE Bond	Kuraray	Self-etch		Self-etching primer	Bond	μTB(hourglass)	41.26	$p < 0.05$	26.77
					NaOCl (5 s)	Self-etching primer	Bond		40.34	$p < 0.05$	31.62
					HOCl 50 ppm (5 s)	Self-etching primer	Bond		41.97	NS	39.28
					HOCl 100 ppm (5 s)	Self-etching primer	Bond		41.24	$p < 0.05$	34.16

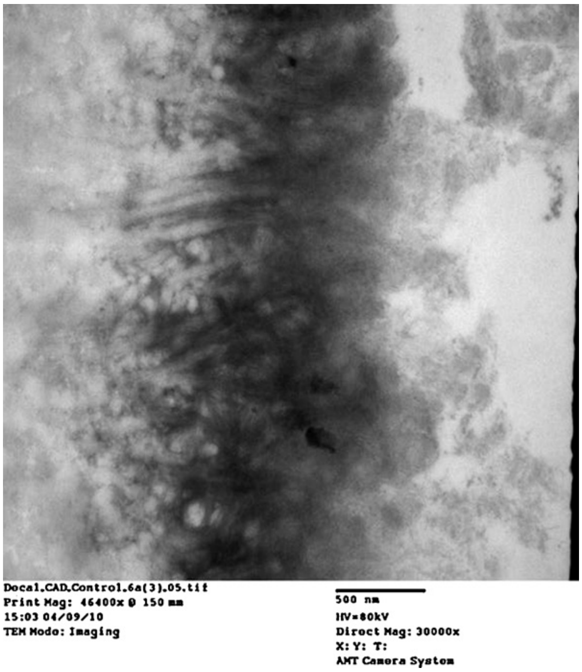

Figure 9 Transmission electron micrograph (TEM) of the adhesive interface of Clearfil SE Bond in caries-affected dentin. The interface exhibited irregular with thicker and more porous hybrid layer, in which hybridized smear layer was seen with the "fuzzy carpet" appearance along the top of the hybrid layer.

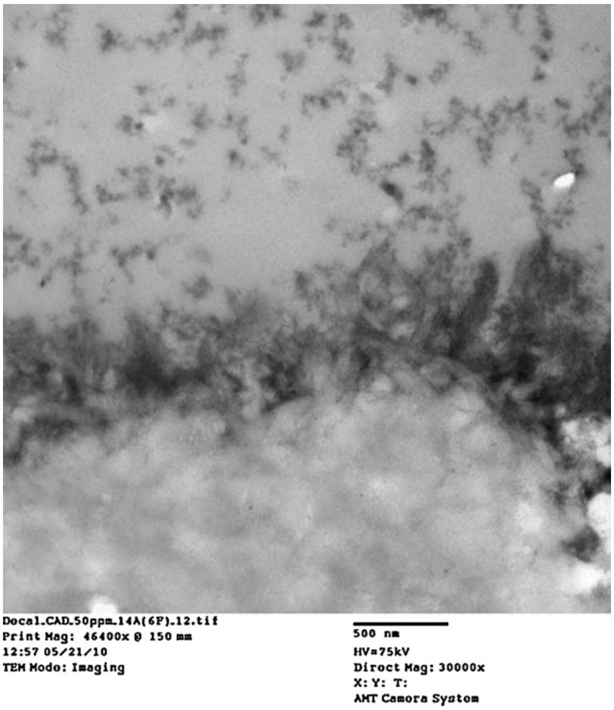

Figure 10 Transmission electron micrograph (TEM) of the adhesive interface of Clearfil SE Bond in caries-affected dentin pretreated with 50 ppm HOCl solution for 5 s. The hybrid layer was thinner and uniform without hybridized smear layer.

Table 3 The review papers concerning about bonding durability to caries-affected dentin.

Author	Ref.	Adhesive material	Manufacturer	Bonding system	Bonding procedure	Test method	Degradation stress	Normal dentin			Caries-affected dentin		
Nakajima et al. (2006)	[47]					mTB (hourglass)	Storage with hydrostatic pulpal pressure	24 h		1 month	24 h		1 month
		Clearfil SE Bond	Kuraray	Self-etch	2-Step			47.3	$p < 0.05$	29.4	31.4	NS	28.3
Omar et al. (2007)	[46]					mTB(stick)	Thermocycling	Before		After	Before		After
		Scotchbond MP	3 M	Etch and rinse	3-Step			22.19	$p < 0.05$	15.7	18.6	NS	16.62
		Clearfil SE Bond	Kuraray	Self-etch	2-Step			24.25	NS	22.3	20.7	NS	20.23
		Xeno IV	Dentsply/ Caulk	Self-etch	1-Step			21.43	NS	18.3	15.45	NS	14.8
Erhardt et al. (2007)	[40]					mTB (hourglass)	Storage in water	24 h		6 months	24 h		6 months
		Scotchbond 1	3 M	Etch and rinse	2-Step			42.6	NS	38.4	34.5	$p < 0.05$	27.8
		Clearfil Protect Bond	Kuraray	Self-etch	2-Step			39.2	NS	39.5	28.7	$p < 0.05$	24.5
		AdheSE	Ivoclar Vivadent	Self-etch	2-Step			28.2	NS	27.2	24.2	$p < 0.05$	17.2
Komori et al. (2009)	[45]					mTB(beam)	Storage in artificial saliva	24 h		6 months	24 h		6 months
		Scotchbond MP	3 M ESPE	Etch and rinse	3-Step			[a]	$p < 0.05$	[a]	[a]	NS	[a]
		Scotchbond MP with 2%CHX					[a]	NS	[a]	[a]	NS	[a]	
		Single Bond 2	3 M ESPE	Etch and rinse	2-Step			[a]	$p < 0.05$	[a]	[a]	$p < 0.05$	[a]
		Single Bond 2 with 2%CHX						[a]	$p < 0.05$	[a]	[a]	NS	[a]

dentin after 6-month storage in artificial saliva, but it did not alter the bond strength of caries-affected dentin.

Thermocycling showed no significant effects on the bond strength of 3-step etch and rinse system to caries-affected dentin, although there were significant reductions in bond strength to sound dentin. Moreover, for 1-step and 2-step self-etch adhesives, no significant effect on bond strength was detected when bonded to sound and caries-affected dentin [46].

Fluid penetration into the resin—dentin interface occurs *via* dentinal tubules under constant hydrostatic pulpal pressure, as well as *via* the dentin margin. Therefore, the presence of mineral deposits in dentinal tubules may alter the bonding durability between normal and caries-affected dentin. Nakajima et al. [47] reported that constant hydrostatic pulpal pressure during 1-month storage significantly decreased the bond strength of 2-step self-etch system to normal dentin, but did not affect the bond strength to caries-affected dentin. The lower dentin permeability of caries-affected dentin may therefore reduce water penetration into the interface, leading to long-term stability of the interface when there is no direct exposure to water in presence of the surrounding bonded enamel. Tubular occlusion may prevent water entrapment, being manifestations of evaporative and convective water flux from dentin, at the resin—dentin interface [49]. Current one-step self-etch adhesives show higher hydrophilicity, and attract water from the hydrated dentin substrate during application on the adhesive surface and absorb water even after polymerization. Ultrastructurally, water entrapment in the 1-step self-etch adhesive layer is observed in the bonded normal dentin specimen as water-filled channels (i.e. water-tree, water-droplet), however water-treeing and water-droplet formation can be eliminated in the bonded caries-affected dentin specimen [49]. In the absent of water fluxes from caries-affected dentin, a one-step self-etch adhesives might initially establish a better seal along the interface. However, the absorbed water in the adhesive layer would cause hydrolytic degradation of resinous materials over time, compromising the integrity of the resin—dentin interface.

Effect of caries removal methods on bonding to caries-affected dentin

Some researchers have evaluated the effect of caries removal method on bonding to caries-affected dentin [50,51]. Using etch and rinse system of Single Bond (3M), caries removal methods (steel bur in a slow-speed handpiece, air abrasion with aluminum oxide particle, partially diamond-coated oscillating tip with airscaler, hand excavator with Carisolv) did not affect the bond strength to caries-affected dentin [50]. This result is in agreement with another study using etch and rinse system of OptiBond Solo Plus Total-Etch (Kerr), in which there were no significant differences in bond strength to caries-affected dentin between excavation by a steel round bur in a slow-speed handpiece, Er:YAG laser and 600-grit SiC paper [51]. On the other hand, in this study, the 2-step self-etching system of Clearfil Protect Bond (Kuraray Medical) exhibited lower bond strength to caries-affected dentin excavated by steel round bur than Er:YAG laser and 600-grit SiC paper. These results indicate that adhesion to caries affected dentin might be influenced by the caries-removal method in conjunction with the adhesive system used.

Conclusion

Caries-affected dentin is very different in morphological, chemical and physical characteristics from normal dentin. Clinically, resin composite is bonded into a prepared cavity after removal of caries-infected dentin, in which the cavity floor commonly consists of caries-affected dentin with lower bonding efficacy. The intrinsic weakness of caries-affected dentin may not be a clinical problem, if there is surrounding normal dentin and/or enamel that can provide high bond strength to the adhesives [6]. However, given that adhesion to the cavity floor is strongly influenced by the contraction stress of the resin composite, low bonding efficacy to caries-affected dentin would cause further deterioration of the adhesive interface at the cavity floor in the restored cavity. In addition, when exposed the adhesive interface of caries-affected dentin in oral environment, the poor quality of the hybrid layer of caries-affected dentin would compromise the longevity of the composite restoration due to hydrolysis of the resin and collagen fibrils. The specific composition in adhesives may affect bonding to caries-affected dentin. However, improvement effect of composition in adhesives on bonding to caries-affected dentin is unclear. One study [3] compared the bond strengths of Scotchbond Multi-Purpose (3M) with and without polyalkenoic acid copolymer in the primer. It was reported that the polyalkenoic acid in the primer contributed to high bond strength to caries-affected dentin [3]. The improvement of bonding potential to caries-affected dentin should be considered in new development strategies of adhesive materials and carious treatment, which could lead to reinforcement of tooth-composite restoration complex, protecting secondary caries and tooth fracture.

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