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ORIGINAL ARTICLE

Short- and long-term *in vitro* study of the bonding of eight commercial adhesives to normal and deproteinized dentin

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Abstract

Objective. The aims of this study were to investigate the influence of deproteinization of dentin on the shear bond strength (SBS) mediated by eight dentin adhesives, and to evaluate the long-term durability of the SBSs. The hypotheses were that deproteinization of dentin would not affect the capacity for adherence, and that in contrast to the SBSs to collagen-rich surfaces, the SBSs to deproteinized surfaces would be stable during a 1-year period of storage in water. ***Material and Methods***. Ground surfaces of human dentin were either rinsed with water (normal dentin) or treated with sodium hypochlorite (deproteinized dentin). The dentin surfaces were analyzed by Fourier transform-infrared spectroscopy (FT-IR) using horizontal attenuated total reflectance (HATR). In addition, the SBS to normal and deproteinized dentin treated with the adhesives was measured after 24 h or 1 year of storage in water. ***Results***. The IR absorption peaks at approximately 1,640, 1,560, and 1,240 cm^{-1} were assigned to the collagen matrix and peaks at about 1,000 cm^{-1} were assigned to the phosphate group in hydroxyapatite. From the relative magnitude of the peaks, it was determined that the utilized deproteinization method was effective. Furthermore, the normal dentin group showed SBS values ranging from 10 to 39 MPa and the deproteinized dentin group showed SBS values ranging from 13 to 30 MPa. ***Conclusions***. According to the statistical analysis, the results only partly supported the hypotheses: it was found that the influence on bond strength of deproteinization of dentin surfaces and the effect of 1 year of storage in water depended on the composition of the dentin adhesive.

Key Words: *Adhesives, bond strength, deproteinized dentin, FT-IR analysis, long-term durability*

Introduction

In the past decade, a few dental adhesives have been commercialized with the aim of increasing the bonding efficacy and simplifying the bonding process. The mechanisms involved in the adhesion of resin composite to enamel and dentin are of a different nature. In 1955, Buonocore [1] introduced the acid etch technique as a means of obtaining a bond to enamel. Micro-mechanical interlocking between enamel and resin is the key factor in enamel bonding, although recent studies have suggested the possibility of chemical bonding to enamel [2–4].

The hybrid layer is an important prerequisite for mechanical adhesion to dentin. Since Nakabayashi et al. [5] proposed the formation of the hybrid layer in 1982 this layer is believed to be the main factor involved in the mechanism of dentin adhesion. The ideal hybrid layer is created by the penetration of adhesive monomers into superficially demineralized dentin and subsequent polymerization of the adhesive [6]. Whereas the hybrid layer is important for the mechanical adhesion to dentin, Asmussen & Uno [7] have suggested that chemical reactions may contribute to the adhesion to dentin. They hypothesized that a chemical reaction requires compatibility between dentin or conditioned dentin and adhesive resin with respect to polarity and solubility parameters. Fukuda et al. [8] found that the molecular structure of polyalkenoic acids significantly influences the chemical bonding efficacy to hydroxyapatite-based substrates. They also hypothesized that micro-mechanical attachment might provide resistance to acute de-bonding stress, whereas additional

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chemical bonding might be beneficial in terms of sealing. Furthermore, Ikemura et al. [9] and Yoshida et al. [10] characterized some functional monomers with chemical bonding efficacy to hydroxyapatite. However, dentin substrates comprise not only hydroxyapatite but also a collagen matrix.

A number of studies used dentin treated with sodium hypochlorite considering the collagen fibrils as the clue to dentin adhesion [9,11–17]. Vargas et al. [11] suggested that removal of the collagen layer would allow better resin penetration into dentin. They concluded that the collagen layer might not be crucial for the mechanism of adhesion between resin and dentin. By NaOCl treatment of dentin, Pioch et al. [13] determined the influence of the presence of the hybrid layer on the occurrence of nanoleakage. They concluded that commercially available bonding systems were not optimized with respect to adhesion to NaOCl-treated dentin surfaces, although the NaOCl treatment prevented nanoleakage. Munksgaard [15] compared bond strengths by using dry or wet, acid-etched dentin and dry or wet, acid-etched and deproteinized dentin in order to evaluate the efficacies of dentin adhesives. It was hypothesized that low technique sensitivity of an adhesive might be linked to its ability to wet and adhere to collapsed collagen fibers and to the surface of the underlying mineralized tissue.

Regarding the stability of the bond to dentin, several studies have measured the influence on bond strength of long-term storage of the bonded specimens in water [18–20]. It has been hypothesized that part of the degradation in bond strength observed in some of these studies is due to the hydrolysis of collagen fibrils not infiltrated and protected by the adhesive [18,21]. It is therefore conceivable that deproteinized dentin surfaces, where the hybrid layer is reduced or missing, perform better in long-term tests of bond strength. Likewise, with self-etching adhesive systems the etching takes place simultaneously with the infiltration of adhesive monomer [22] so that the presence of unprotected collagen is minimized.

The aim of the present study was to analyze dentin surfaces before and after treatment with a deproteinizing agent with respect to content of collagen. A further objective was to determine the short- and long-term bonding to normal and deproteinized dentin mediated by eight conventional or simplified dentin adhesives. The hypotheses were 1) that deproteinization of dentin would not affect the capacity for adherence, and 2) that in contrast to the shear bond strengths (SBSs) to collagen-rich surfaces, the SBSs to deproteinized surfaces would be stable during a 1-year period of storage in water.

Material and methods

FT-IR analysis

Ten extracted human molars stored in 0.5 wt% chloramine-T solutions were sectioned into 1.2 mm-thick slabs with a low speed diamond saw (Buehler, Lake Bluff, Ill., USA). One to three slabs were obtained from each tooth, resulting in a total of 15 slabs. The slabs were ground flat on #1000 wet SiC paper and stored in water until Fourier transform infrared spectroscopy (FT-IR) analysis. The first recording of a spectrum was performed on ground and water rinsed, but otherwise untreated, dentin surfaces (normal dentin). After the recording, the dentin surfaces were acid-etched with 35 wt% phosphoric acid (diluted from 85 wt% orthophosphoric acid; E. Merck, Darmstadt, Germany) for 20 s, rinsed with water for 15 s and a second IR spectrum was recorded. The third recording was performed after deproteinization according to the previous study by Munksgaard [15]. The dentin slabs were immersed in a stirred aqueous solution of 0.5 vol% sodium hypochlorite (pH ~10.3, Dan-Dental A/S, Vallensbæk, Denmark) for 1 h followed by rinsing with water for 15 s. The dentin slabs were blot dried before FT-IR analysis. Each dentin condition was recorded on five dentin slabs at a time and the recordings carried out in triplicate (Figure 1). The FT-IR spectrometer (Spectrum One; Perkin-Elmer, Norwalk, Conn., USA) was used with the horizontal attenuated total reflectance technique (HATR) accessory fitted with a ZnSe crystal, which was adapted to the dentin surfaces under pressure. The spectra of the slabs were obtained under the following conditions: Range 650–4000 cm^{-1}; resolution 4 cm^{-1}; scan speed 0.2 cm/s; number of scans 10; entrance angle of light beam 45°. The depth of penetration of the beam was calculated to be about 1 μm. After spectral acquisition, the spectra were averaged to enable comparisons between the different dentin conditions.

SBS test

Extracted human molars stored in 0.5 wt% chloramine-T solutions were embedded in slow-curing epoxy resin (EpoFix; Struers, Copenhagen, Denmark) and stored in water until use. The samples were ground on wet SiC paper from #80 to #1000 until flat dentin surfaces appeared and then randomly divided into 32 groups of 8 for each. The dentin surfaces were treated in two ways before application of adhesive. The composition of the proprietary adhesives is described in Table I.

Normal dentin. After grinding, the dentin surfaces were treated with the eight commercial adhesive

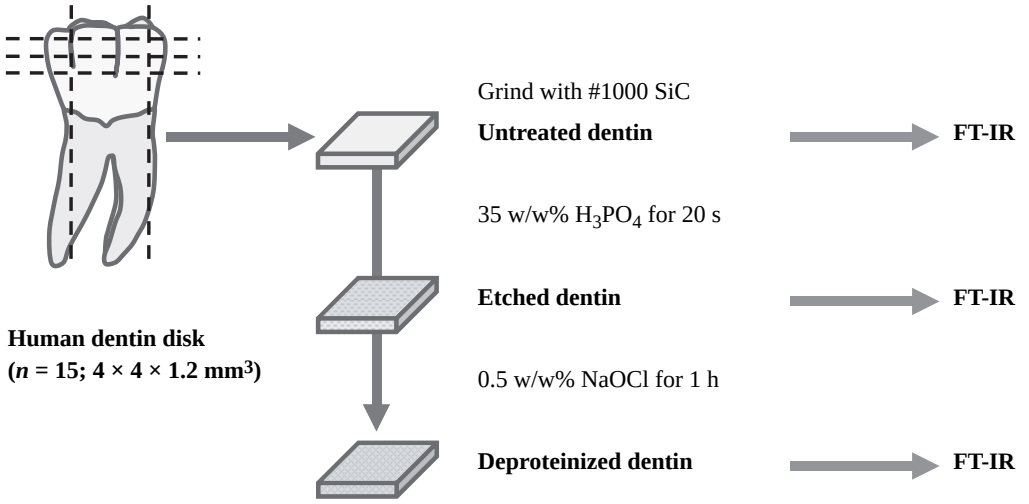

Figure 1. Schematic illustration of the procedure for Fourier transform-infrared spectroscopy FT-IR measurement.

systems. The adhesives comprised one three-step system, four two-step systems (one etch-and-rinse system and three self- etching systems), and three one-step systems, and were applied according to the manufacturers' instructions. The adhesive resin was cured with a halogen light source (XL 3000; 3M, St. Paul, Minn., USA).

Deproteinized dentin. The ground dentin surfaces were deproteinized in accordance with the method described above [15]. The specimens were rinsed with water for 20 s, stored in water until use, and then blot-dried for a few seconds. The adhesives were applied as described above.

A split cylindrical Teflon mold (diameter 3.6 mm, height 2.5 mm) was clamped to the adhesive-treated dentin surface and filled with a resin composite (Filtek Supreme; 3M ESPE). The resin composite was light-cured for 40 s with the halogen light source (400 mW/cm^2). The specimens were removed from the mold after 10 min and stored in water at 37°C for 24 h or 1 year before SBS testing. The SBS test was performed at a crosshead speed of 1 mm/min

Table I. Composition of the commercial adhesive systems

Type	Code	Brand (lot number)	Composition
3-step etch-and-rinse	OF	OptiBond FL[a] (307014)	Etching agent: 37% phosphoric acid FL Primer: HEMA, GPDM, PAMM, ethyl alcohol, CQ, water FL Adhesive: BisGMA, HEMA, GDM, CQ, filler
2-step etch-and –rinse	EL	EXL#628[b] (628)	Etching agent: 35% phosphoric acid DMA, HEMA, polyalkenoic acid copolymer, photoinitiators, ethanol, water
2-step self-etch	OS	OptiBond SOLO Plus[a] (304923)	Self-Etch Primer: HFGA-GDM, GPDM, ethanol, MEHQ, EHDMAB, CQ Adhesive: BisGMA, HEMA, GDM, GPDM, CQ, ethanol
	CS	Clearfil SE Bond[c] (41264)	Primer: MDP, HEMA, hydrophilic DMA, CQ, N,N-diethanol p-toluidine, water Bond: MDP, BIS-GMA, HEMA, hydrophilic DMA, CQ, N,N-diethanol p-toluidine
	AS	AdheSE[d] (F21254)	Primer: Phosphoric acid acrylate, bis-acrylamide, water Bond: DMA, HEMA, filler
1 step self-etch	IB	iBond[e] (010048)	UDMA, 4-META, glutaraldehyde, acetone, water
	PL	Adper Prompt L-Pop[b] (156660)	Methacrylated phosphoric esters, polyalkenoic acid copolymer, fluoride complex, photoinitiators, water
	XE	Xeno[f] (0305001867)	A: HEMA, water, ethanol, BHT, filler B: phosphoric acid modified methacrylate, MFPM, UDMA, BHT, CQ, DABE

HEMA = hydroxyethylmethacrylate; GPDM = gycerophosphate dimethacrylate; PAMM = mono (2-methacryloxyethyl) phthalate; CQ = camphorquinone; BIS-GMA = bisphenol A glycidyl dimethacrylate; GDM = glycerol dimethacrylate; HFGA-GDM = hexafluoroglutaric anhydride; MEHQ = 4-methoxyphenol; EHDMAB = 2-ethylhexyl-4-dimethylamino benzoate; DMA = dimethacrylate; MDP = 10-methacryloyloxydecyl dihydrogenphosphate; UDMA = urethane dimethacrylate; 4-META = 4-methacryloxyethyl trimellitate anhydride; BHT = butylated hydroxy toluene; DABE = ethyl 4-dimethylaminobenzoate; MFPM = monofluorophosphazene modified methacrylate resin.
[a]Kerr, Orange, Calif., USA; [b]3M ESPE, St. Paul, Minn., USA; [c]Kuraray Medical, Tokyo, Japan; [d]Ivoclar Vivadent, Schaan, Liechtenstein; [e]Heraeus Kulzer, Hanau, Germany; [f]Dentsply, Konstanz, Germany.

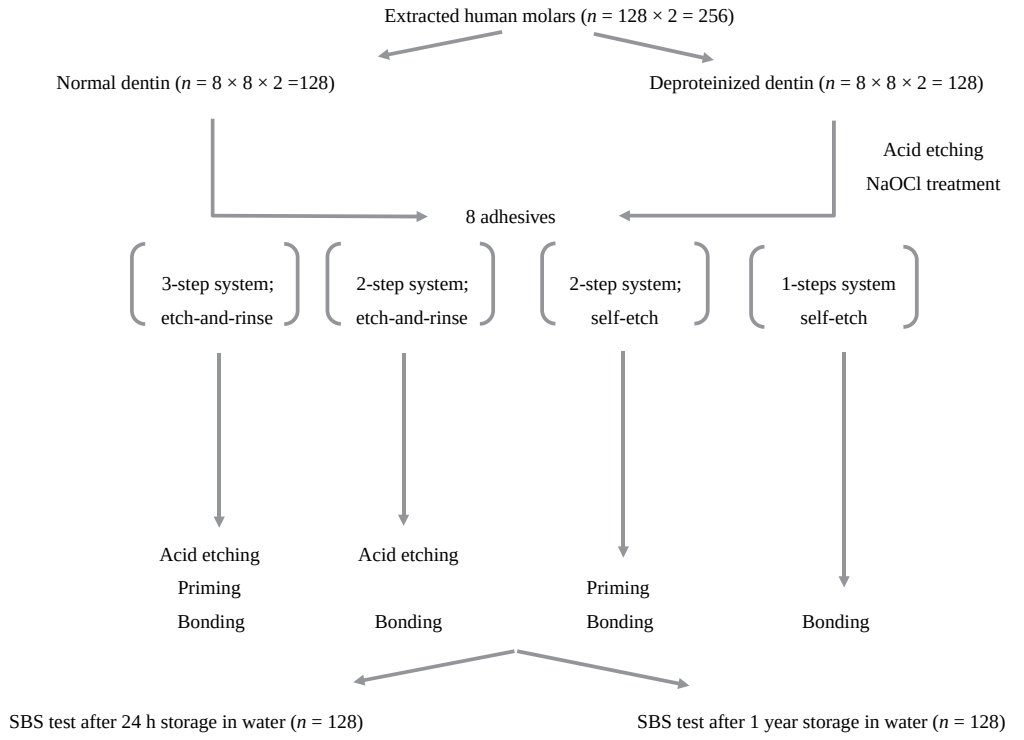

Figure 2. The procedures for each adhesive system.

with a Universal Testing Machine (Instron, High Wycombe, UK). The procedures for each system are shown in Figure 2.

Statistical analyses

The results of the SBS test were analyzed with three-way and two-way ANOVA with adhesive, storage period, and dentin condition as independent variables. Multiple comparisons were performed with Tukey's HSD test. The statistical analyses were carried out at a level of significance of 5%.

Results

FT-IR analysis

The results are summarized in Figure 3. The bands relevant for the study could be identified on the basis of previous investigations [9,23–26]. The strong and broad absorption bands at 3200–3400 cm^{-1} were assigned to NH- and OH absorption including absorption by water. The absorption bands at 1637 cm^{-1} (amide I), 1559 cm^{-1} (amide II), and 1240 cm^{-1} (amide III) were assigned to dentinal collagen. In view of the presence of water in the only blot-dried dentin surfaces, the band centered at 1637 would most probably have a contribution from the HOH bending vibration at 1648 cm^{-1} [9]. The bands at 998 and 1014 cm^{-1} (phosphate) were assigned to the apatite phase of dentin. The normal dentin surface (polished with #1000) showed amide I band at 1637 cm^{-1} and a comparatively strong phosphate band at 998 cm^{-1}. After acid etching, the intensity of collagen bands (1637, 1559 and 1240 cm^{-1}) was increased relative to the phosphate band (about 1014 cm^{-1}). A relatively small band, as compared to the phosphate band at 1014, was detected after deproteinization at 1637 cm^{-1} but the collagen bands at 1559 and 1240 cm^{-1} had disappeared.

Shear bond strength

The results are shown in Table II. Three-way ANOVA revealed a significant difference between adhesives ($p < 0.001$), significant interaction between adhesives and storage period ($p = 0.001$), and significant interaction between adhesives and dentin condition ($p < 0.001$). For each adhesive, two-way ANOVA examining the influence of storage period and dentin condition showed a significant interaction for AS. There was an independent influence of both storage period and dentin condition for OS and a significant influence of storage period for XE. For the other adhesives, no significant influence of storage period and dentin condition was found.

Discussion

The FT-IR analysis showed a significant reduction of the phosphate band as a consequence of the acid etching, in agreement with earlier studies [27]. This indicates the powerful demineralizing capacity of 35 wt% phosphoric acid. The FT-IR analysis further showed that the employed method of deproteiniza-

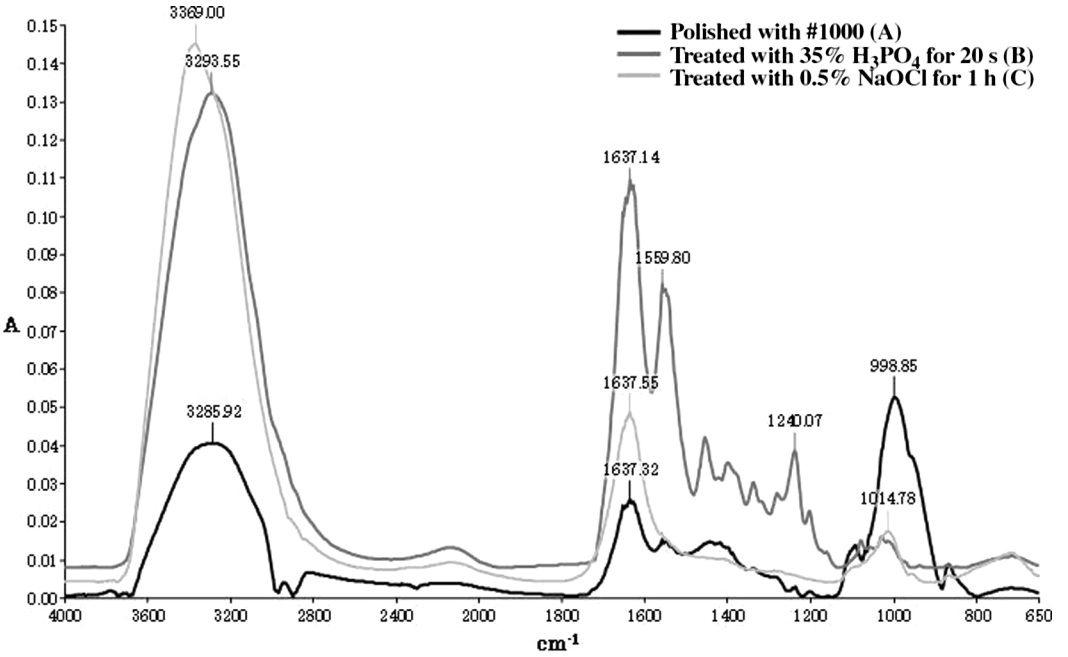

Figure 3. FT-IR spectra of untreated dentin (A), etched dentin with 35 w/w% H_3PO_4 for 20 s (B) and deproteinized dentin with 0.5 w/w% NaOCl for 1 h (C).

tion removed the collagen from the surface of the dentin to a large extent. In the study by Ikemura et al. [9], the dentin surfaces were treated with 5 wt% NaOCl for 10 and 30 min to remove the collagen fibrils. The amide II completely disappeared from the FT-IR spectra as a consequence of this treatment. Although concentration and treatment time were not the same, this is in agreement with the present study, which also showed the disappearance of the amide II band. The band at 1637 cm^{-1} was assigned to amide I. However, the presence of this band after the NaOCl treatment would seem to indicate the interference of water, and not necessarily that deproteinization, although extensive, was not complete. Another effect of hypochlorite treatment that may play a role in dentin bonding is a morphological change into a rougher surface texture [28]. However, the oxidizing potential of prolonged NaOCl treatment should not be overlooked since it has been found that such a treatment may have a detrimental effect on bonding [29], although this was not evident in the present study. Treatment with 0.5 vol% NaOCl for 1 h is obviously not clinically relevant, but even so may be useful for evaluating the efficacies of dentin adhesives [15]. Furthermore, it may lead to a better understanding of bonding mechanisms in view of future improvements in dentin adhesives.

Table II. Shear bond strength (MPa) to normal and deproteinized dentin obtained with eight proprietary adhesive systems after 24 h and a 1-year period of water storage. Mean values (SD)

Code	Type of dentin	Storage period	
		24 h	1 year
OF	Normal dentin	31 (4.7) a	28 (6.8) a
	Deproteinized dentin	27 (4.2) a	25 (7.0) a
EL	Normal dentin	20 (7.6) b	22 (7.1) b
	Deproteinized dentin	16 (6.4) b	16 (4.7) b
OS	Normal dentin	13 (2.4) c	12 (4.5) c
	Deproteinized dentin	22 (4.8) e	16 (2.5) d
CS	Normal dentin	39 (4.4) f	30 (10.0) f
	Deproteinized dentin	30 (7.4) f	28 (9.6) f
AS	Normal dentin	17 (4.3) g	25 (9.6) g, h
	Deproteinized dentin	27 (6.7) h	26 (2.4) h
IB	Normal dentin	10 (4.5) i	16 (4.0) i
	Deproteinized dentin	15 (3.9) i	16 (7.5) i
PL	Normal dentin	14 (4.1) j	13 (3.0) j
	Deproteinized dentin	13 (2.8) j	14 (3.4) j
XE	Normal dentin	26 (5.4) l	20 (5.8) k
	Deproteinized dentin	26 (5.6) l	17 (4.7) k

For each adhesive, values with the same letter are not different at $p = 0.05$.

Bonding to dentin is dependent on diffusion of resin monomers into the dentin surface [24]. Wege et al. [17] characterized the effect of grinding, acid etching, and deproteinization on the wetting ability of dentin. They found an effect on contact angle which indicated that acid etching and deproteinization increased the wetability of dentin. Inai et al. [12] evaluated the effect of sodium hypochlorite treatment on bond strength using several dentin-bonding systems. Their findings suggest that the bonding systems containing acetone interact strongly with etched and deproteinized surfaces because the adhesive may readily impregnate the resulting porous dentin surfaces. The results of Munksgaard's study [15], which showed higher or unaltered strength on deproteinized dentin compared with normal etched dentin, were explained by a higher lipophilicity of the deproteinized surface, which might better match that of the bonding agents and resin composite.

An examination of the compositions of the adhesives (Table I) will reveal that all commercial adhesive systems contain phosphate, phosphonate or carboxylic groups. In theory, such groups are capable of reacting or interacting with Ca-ions of the apatite on the dentin surface. Thus, higher bond strengths to the deproteinized dentin might be expected. In this study, only the SBS of OS to the deproteinized dentin was higher than to the normal dentin. The initially higher SBS of AS was not detected after long-term water storage. The SBSs of the other systems were not affected by the deproteinization. Thus, a possible effect of a chemical component of the bonding is not obvious.

Decrease in bonding effectiveness by long-term water storage is supposedly caused by degradation of interface components by hydrolysis of resin or collagen [21]. In the present study, a reduction in SBS was observed only with OS and XE. Both adhesive systems are of the self-etching type. Furthermore, with the etch-and-rinse systems OF and EL, there was no indication that the deproteinized surfaces resisted degradation of the bond better than did the normal dentin surfaces. The results, therefore, do not lend credit either to the assumption that simultaneous etching and infiltration is an important parameter in dentin bonding or to the idea that unprotected collagen is the weak link in a bonding system. However, it may be that a storage time of only one year was not sufficient to show a difference. Although the susceptibility to degradation of the polymer of a dental adhesive has not yet been clarified in terms of chemical structure, the chemical compositions of monomers or solvents of the adhesives may affect the longevity of the bonds in a humid environment [30]. Therefore, further research will be required to evaluate the durability of the adhesive interface and the influence of sodium hypochlorite treatment on long-term degradation of the bond to dentin by using not only commercial adhesives but also experimental ones with well-defined compositions.

The FT-IR analysis showed that acid etching and deproteinization changed the relative amounts of collagen and apatite in the dentin surface. In the present study no systematic differences in short-term bond strength to collagen-rich and deproteinized dentin were found, in that only two of the eight systems showed a higher strength to deproteinized dentin. This means that the first hypothesis will have to be accepted, in part. Regarding long-term stability of the bond to deproteinized dentin, again, no systematic differences in bond strength to collagen-rich and deproteinized dentin were found. The water storage gave rise to a reduction in SBS to deproteinized surfaces with two of the eight systems and to a reduction in SBS to collagen-rich surfaces with one system. As a consequence, the second hypothesis will have to be accepted, but also only in part. On the basis of the composition of the adhesive systems, it is, however, not easy to understand which factors are decisive in this respect. The findings may be associated with either the surface free energy of treated dentin [12,17] or the pKa values for the collagen functional group [31]. It would seem that further analyses are indispensable for the understanding of a possible chemical bonding to dentin and the durability of the bond.

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