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Fluid flow through dentin–self-etch resin interface during long term in vitro aging

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ABSTRACT

This work aimed at characterizing the interface between dentin and the resin-infiltrated dentin made following the etching procedure that prepares for the bonding of tooth-colored restorations. The non-destructive measurement of fluid flow through the dentin–self-etch resin interface was followed repeatedly during a two year aging period. Two self-etch adhesive systems were selected for experiments on the evolution of permeability and evaluation of infrared spectral changes following the 24 month aging period. The adhesives contained water and a co-solvent, namely acetone for iBond, and t-butanol for Xeno V. For both adhesive systems, the permeability decreased during the first 3 months after etching, reaching values of −66.9 and −70.5% for iBond and Xeno V, respectively. Afterwards, the fluid flow slowly increased but still remained below 50% of the initial value following the 2-year aging period. The slow degradation of the resin–dentin interface, attributed to water impregnated collagen hydrolysis, is evidenced by these variations in fluid flow, and is also noted by the increase in water-related infrared absorption bands at 3300 cm^{-1} and at 1600 cm^{-1}. The results are discussed in terms of co-solvent hydrophobicity, evaporation rate and viscosity together with resin infiltration depth and affinity for water.

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1. Introduction

Aging of biomaterials is a topic of continuing interest. In the case of dental restorations, contemporary biomaterials and methods have aimed at simplifying procedures and obtaining an esthetic dental tissue repair within a short operating time. However the long term integrity of teeth restored with modern materials is as important as the immediate result. Clinical studies as well as experimental work have revealed that some simplified one-step procedures using self-etch adhesives to bond composite restorations tend to degrade to the point where new restorations have to be made [1–3]. The weak spot in bonding composites to dentin has been identified as the demineralized water-soaked collagenous tissue resulting from smear layer removal by the acid etching step preceding the resin infiltration. Demineralized collagen exposed to biological fluids may be hydrolyzed by matrix metalloproteinase. This results with time in hydrolysis of the base of the tooth restoration, with possible infiltration of bacteria at the interface between healthy dentin and biomaterials. To prevent hybrid layer decay, several methods have been proposed [4,5], but an essential step is to replace dissolved hydroxyapatite by a hydrophobic, water resistant polymer that infiltrates and surrounds collagen fibrils as much as possible. This will preserve the biomaterial–dentin interface from subsequent deterioration. However, the demineralizing step requires an aqueous medium for acid expression and hydroxyapatite dissolution. Drying of the wet demineralized collagen results in collagen fibril collapse [6], and such observations have led to the development of ethanol based self-etch adhesives [7–11]. Indeed the acid monomers used in removing the smear layer and preparing the dentin are soluble in organic solvents. A polar medium is yet required for ion dissolution so that all self-etch adhesives also contain some water.

Previous work has focused on the determination of the penetration depth of the organic monomers with respect to the depth of dentin demineralization, mostly by microscopic observations [12]. Justification for the use of self-etch adhesives lies in the proposal that the acid penetrates to the same depth as the accompanying monomer, so that little hiatus should remain between the sound dentin and the polymerized resin. Experimental work mostly centered on micromechanical testing of various dentin to resin interfaces has nevertheless illustrated the weakening of the biomaterial bonding to dentin [13]. Pashley and Livingston [14] have developed an in vitro method to measure fluid flow under pulpal pressure through dentinal tubuli. This method uses a split-chamber device to measure dentin permeability, and has been used to determine the effect of desensitizing agents [15]. Several authors have used permeability measurements to evaluate adhesive system effectiveness in completely

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penetrating the etched dentin and investigating the durability of the dentin–resin bond [16–18].

The aim of the present study was to use the non-destructive permeability measurement technique to repeatedly measure fluid flow through treated dentin disks in order to highlight any variations that reflect the aging effects for long time periods. Two adhesive systems were selected, each containing a co-solvent: iBond (water/acetone), and Xeno V (water/t-butanol). Variations in dentinal permeability were monitored in vitro by measuring fluid flow through human dentin slices of constant thickness subjected to pulpal pressure. To avoid other confounding factors such as thermal expansion coefficient miss-match, the samples were stored at room temperature over a 2 year period.

The null hypothesis was that there would be no differences in permeability according to aging time for the two systems tested. On the other hand, any differences observed would validate the use of permeability measurements to study the long term properties of adhesives and relate this to aging effects.

2. Materials and methods

The two adhesive systems tested in this study were: iBond (Heraeus Kulzer, Hanau, Germany), and Xeno V (Dentsply, Konstanz, Germany). They were kept refrigerated for conservation prior to use (see Table 1).

Twenty sound human third molars extracted from 18- to 25-year-old patients for pathological reasons were used in this study. They were randomly assigned to two groups of 10 teeth used to monitor dentin permeability during the 24 months following the application of the same adhesive systems, each applied to one of the 2 groups of 10 teeth.

All teeth were subjected to the same initial preparation procedure. Dentin slices of 1 mm thickness were obtained by sawing the crown between the enamel and pulpal region with cuts parallel to the occlusal surface, using a slow speed water-cooled diamond disk saw (Isomet 2000, Buehler GmbH, Düsseldorf, Germany). The deep dentin was chosen to promote adhesive system infiltration into the demineralized dentin, an ideal condition for evaluating resin–dentin interaction mechanisms.

The dentin slices were etched on their occlusal and pulpal sides during 15 s with 36% phosphoric acid (Conditioner 36, Dentsply, Konstanz, Germany) to remove the smear layer formed during sawing, then rinsed for 30 s. The etched dentin slices were then centered on a polycarbonate ring with a 6 mm inner diameter hole and glued on the pulpal side using an epoxy glue (Araldite, Ciba, Sodiema, Coubert, France). The assembled elements were dried 24 h before testing. For all samples, 3 hydraulic conductance measurements (Fig. 1) were made at different times:

Table 1
Composition of the adhesives studied as given by manufacturers.

Adhesive systems	Origin	Composition	Solvent	Batch no.
iBond	Heraeus Kulzer, Hanau, Germany	4-META UDMA Glutaraldehyde Camphorquinone	Water Acetone	010033
Xeno V	Dentsply, Konstanz, Germany	Bifunctional acrylate Acidic acrylate Functionalized phosphoric acid ester Acrylic acid Initiator Stabilizer	Water Tert-butanol	0703001239

Table 2
Application procedure for the self-etch adhesives used.

Adhesive systems	Application procedure
iBond Heraeus Kulzer, Hanau, Germany	Shake bottle briefly. Dispense iBOND Self Etch into the well. Immediately after dispensing apply a copious amount of iBond Self Etch to the entire cavity surface and margin with the applicator tip or brush. After application agitate the adhesive slightly for 20 s. Carefully air-dry iBond Self Etch for 5–10 s. Light-activate iBond Self Etch for 20 s.
Xeno V Dentsply, Konstanz, Germany	Easy squeeze bottle. Dispense 1 or 2 drops of Xeno V into the well. Apply Xeno V sufficiently, wetting all cavity surfaces uniformly. Then gently agitate the adhesive for 20 s. Evaporate solvent by thoroughly blowing with air from an air syringe until there is no more movement of the adhesive, but for at least 5 s. Light-activate for 20 s.

T0: dentin specimen prior to any adhesive treatment. This gave the reference value to compare with any subsequent difference seen on the same sample following treatment.

T1: dentin with calibrated smear layer. The T0 and T1 values were the average of successive measurements taken every 30 s for 15 min. This artificial smear layer was created by gently rubbing the occlusal sides of the dentin slices 50 times on fine sandpaper (P2000 de Buehler).

T2: dentin with adhesive system applied according to the manufacturer's instructions (Table 2). The reported T2 values derived after adhesive system application were the average result of 30-second measurements taken during 15 min. Thereafter, the specimens were aged for 24 months at room temperature (22 ± 1 °C) in the dark in closed vessels with 100% humidity [21,23–25]. Chloramine vapor prevented bacterial proliferation during storage. Hydraulic conductance measurements were made after aging periods of 3 months (T3), 6 months (T4), 9 months (T5), 12 months (T6) and 24 months (T7). To compensate for the large variations observed among different dentin

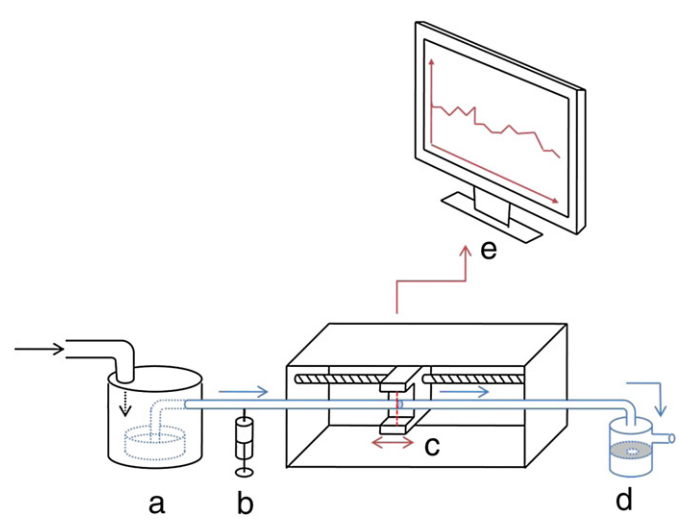

Fig. 1. Hydraulic conductance experimental set-up. The components are a) the pressurized reactor to reach 0.2 bars on a physiological solution pouch; b) a syringe for insertion of an air bubble; c) the Flodec bubble motion analyzer; d) the sample holder where the liquid phase penetrates the dentin slab to be tested; and e) the data recovery and analysis system.

samples, each conductance value was expressed as the % variation of an individual specimen compared to its initial value obtained at T0. Thus each sample had its own reference starting value [19]. The initial fluid flow permeating the dentin slices was evaluated using liquid physiological saline as described in previous publications [20–22].

A time series analysis was performed to assess the stationarity and trend of the data obtained for each adhesive system. The Kwiatkowski–Phillips–Schmidt–Shin (KPSS) test was used to test the data for stationarity. Trends of hydraulic conductance values over time were tested using Spearman's rank correlation rho. Comparisons between adhesive systems were performed using a multiple comparison test (Duncan's test). The significance level was fixed at 0.05. Statistical analyses were conducted using R software (Foundation for Statistical Computing, Vienna, Austria) version 2.7.1, with the additional package series (version 0.10-16) and laercio (version 1.0-0).

Infrared spectra were recorded on a Mattson infrared spectrometer (Genesis II spectrometer for Mattson) by diffuse reflectance on a diamond ATR. The dentin slices were placed on the diamond face with no further sample preparation. Spectra were registered from 500 to 4000 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}. Small sample chips weighting 15 mg were used for the thermogravimetric analysis of water uptake and loss. The samples were placed in platinum holders and analyzed with an SDT Q600 from TA instruments (Guyancourt, France).

3. Results

After a decrease of the hydraulic conductance values during the first three months for the two adhesives (Fig. 2), we observed a non-significant trend for an increase after three months (rho = 0.14, and 0.26 for iBond and Xeno V respectively) (Table 3). At time T1, no statistically significant differences were found between the two adhesives (−41.81 and −42.54%). The smear layer was reproducible but differences in dentin samples justified the use of each sample as its own control. During the first three months, a decrease in permeability was observed for all samples. This improvement was significant for iBond and Xeno V, with Xeno V showing the largest decrease (−70.46%).

Table 3
Hydraulic conductance over time for the adhesive systems.

	Stationarity[a]	Trend[b]		Multiple means comparisons[c]	
	p-Value	Rho	p-Value	Means	Duncan
iBond	>0.1	0.14	0.80	−0.59	a
Xeno V	>0.1	0.26	0.66	−0.61	a

[a] Kwiatkowski–Philips–Schmidt–Shin test for the null hypothesis that values are stationary over time.
[b] Spearman's rank correlation.
[c] Comparisons by Duncan's test: same letters are not statistically different.

The largest improvement in permeability between times T2 and T3 was observed for iBond (from −48.68 to −66.89%). Three months after application, both the adhesives showed better performance than initially. This three-month delay yielded the stronger permeability decreases of the whole 24-month period. Later on, the permeability degraded slowly and progressively, but remained better than the initial value.

The infrared spectra are illustrated in Fig. 3. The most noticeable event seen in the case of iBond, is the increased intensity of the large water stretching vibrations near 3300 cm^{-1} following the 2 year aging period. The carboxyl stretching band at 1700 cm^{-1} also is covered by the strong water vibration band at 1600 cm^{-1} following aging. The phosphate band at 1250 cm^{-1} also decreases in intensity with time. The weight losses attributed to water in the specimens increased by slightly more than 1% after aging (from 9.4 to 10.3% water for iBond and from 9.5 to 10.6% for Xeno V). All the losses were endothermic in nature.

4. Discussion

Hydraulic conductance measurements over the 24-month period revealed relative variations in the permeability as a function of time over this period. The results are presented in Fig. 2. Close examination of the figures shows that the decrease in permeability was not obtained immediately but was acquired slowly over the first three months. We must stress the fact that our samples were maintained in a humid atmosphere. The mechanical properties of adhesives are

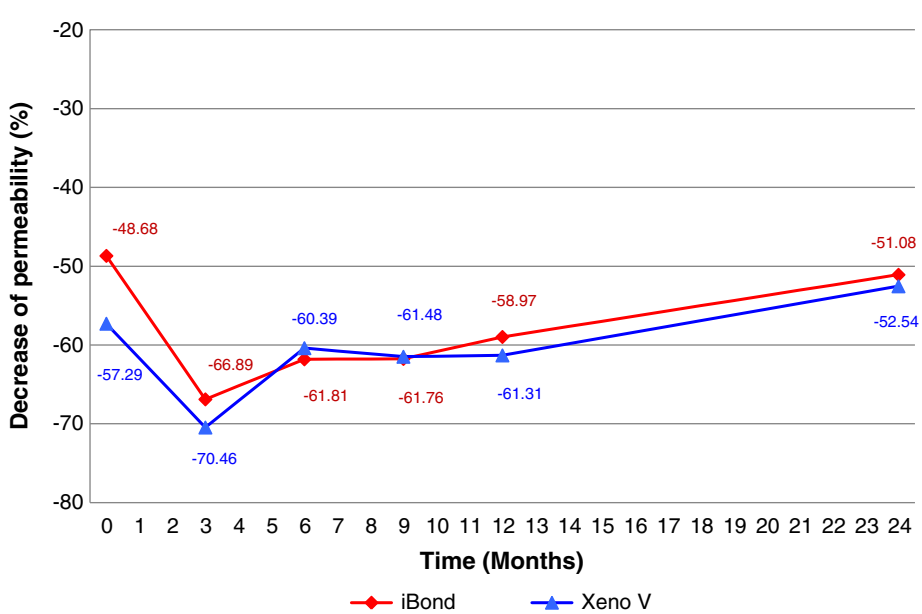

Fig. 2. A representative curve of the permeability for 2 years after application of the adhesive systems.

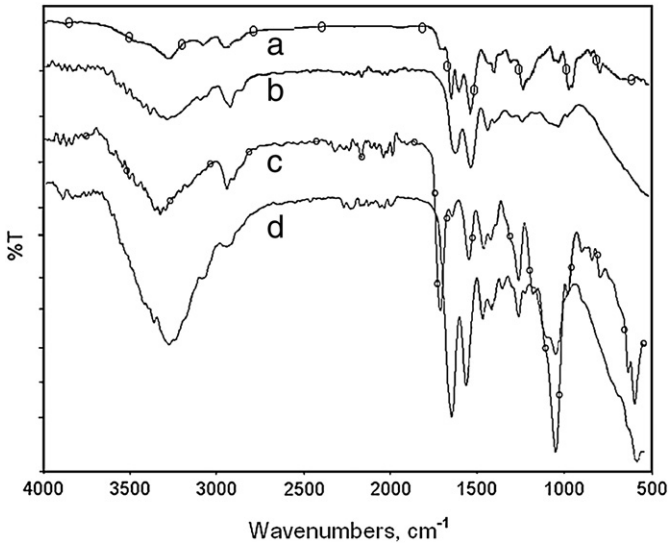

Fig. 3. Infrared diffuse reflectance spectra of Xeno V treated samples immediately after the application of adhesive (spectrum a) and following a 2 year aging period spectrum b). An increased water absorption band is observed near 3300 cm^{-1}, as well as loss of resolution near 1600 cm^{-1} which corresponds to the in plane water bending mode. Spectra of iBond at time = 0 (spectrum c), and of iBond at time = 2 years (spectrum d). Most noticeable is the increase in the intensity of the large water stretching absorption band at 3300 cm^{-1}. The water vibration band at 1600 cm^{-1} also masks the carboxyl stretching frequency at 1700 cm^{-1}. The spectra at time t = 0 are marked with o's.

known to degrade over time in humid conditions [23] whereas they remain stable in dry conditions [24]. This has been related to the presence of hydrophilic monomers, which can absorb as much as 12 wt.% water [25–27], leading to hydrolysis of resins and collagen and consequent loss of mechanical strength [9]. Self-destruction of the collagen matrix infiltrated with water or even mineralized and in the absence of bacteria has been proposed as an explanation [28]. However, it may be possible to stabilize the polar ionic resin groups by allowing biomineralization with nucleation of hydroxyapatite crystals near the ionic bonds of polymers. In the hybrid layer obtained with self-etch resins, the proximity of calcium ions and polymer functional groups may explain their mineralization [29]. Our results clearly show a decrease in permeability during the first three months, followed by a slow loss of impermeability thereafter. This could be ascribed to the slow mineralization of the dentin–polymer interface. Some authors prefer to wait after 24 h of demineralized water storage before measuring adhesive strength in order to attain more stable values [18,30]. Several authors [31–33] did not detect any hybrid layer degradation following 3 months of water immersion, but only much later. The strongest adhesive period could be situated between 24 h and 3 months after application. Alternatively, another explanation could be provided by collagen fibril expansion by progressive water pick-up resulting in a tighter seal, albeit with endogenous water replacing non-evaporated co-solvent, which would diffuse slowly. Our previous investigations have revealed large amounts of solvents in self-etch adhesives [34] and it seems probable that, if these solvents penetrate dentin together with the monomers, they will give way to water replacement with time. It is not so surprising that impermeability takes some time to reach its best results, which may be attributed to more complete polymer formation and relaxation into optimum conformation. However, as pointed out earlier, establishment of gradients seems to be inevitable [35] and, at some point, water will be present in quantities sufficient for a hydrolytic activity. The moment of optimum permeability decrease may be related to the time it takes to remineralize the polar sites and the time when degradation starts [29]. We have previously reported that ethanol wet bonding may improve long term durability by minimizing the presence of water to that needed for keeping collagen in a water bonded conformation [36].

In self-etching adhesives, the main ingredients are functional monomers for polymerization and bi-functional monomers for crosslinking. In addition to unsaturated acrylic double bonds, the monomers contain acidic functional groups (carboxylic acid, phosphate or phosphonate acids), which are intended to dissolve hydroxyapatite. The length of the hydrocarbon chain regulates the hydrophilic or hydrophobic character of the molecule. The difunctional crosslinking monomers with two double bonds allow binding to the composite and prevent excessive polymer expansion. The crosslinking of the polymer matrix confers extra strength on the adhesive by tying polymer chains together. This enhances the hydrophobic character of the polymer. 4-META is the acidic monomer used in iBond. This carboxylic anhydride can covalently bind to collagen [37]. Yet it is not likely to form a calcium salt within clinical time limits [38]. This is related to its weak ionization. 4-META is not so stable in aqueous media because of hydrolysis of the ester functions present between the ethyleneglycol and methacrylate groups and the trimellitic acid. It is one of the least acidic of the acidic monomers and it forms both hydrophilic and hydrophobic bonds.

The functional monomer present in Xeno V is a phosphoric acid ester functionalized with an acrylic acid group. Chemical bonding with hydroxylapatite is feasible in a reasonable time span. The solubility of the calcium salt formed is limited in water [38,39]. The weak point is the ester linkage between the phosphate and the rest of the molecule, which may hydrolyze with time in the presence of water.

Our results show that the two adhesive systems tested lower dentin permeability and that this decrease is maintained with time. Following 2 years of aging, among the products tested, Xeno V had the best capacity to decrease water permeability and maintain this with time. The difference with iBond was significant. Xeno V is different in composition with respect to solvent and to functional monomer type. Phosphoric acid esters are known to be susceptible to water hydrolysis, which separates the acid group from the methacrylate part and may lead to free unbound acid groups in the matrix. On the other hand, the monomer used in Xeno V is “inversely functionalized”. Hydrolysis of the ester in this monomer would not release acid or acrylate groups but only an alcohol molecule. This could explain the improved stability found in our study.

This more stable “inversely functionalized” monomer still has some inconvenient features: other ester functions remain present, particularly the phosphate ester groups which may suffer hydrolysis and separate the methacrylate function from the acidic function. Furthermore, the double bond is no longer in a terminal position but in a more sterically hindered position which may affect the degree of polymerization. Non-polymerized acid functionalized monomers may weaken the mechanical properties of the polymer if they remain mobile in the matrix.

According to Cadenaro [40], the degree of conversion of monomers depends on the type of monomer and type of solvent, with better infiltration given by mixed solvents. Water is needed for acidity expression [41] but should not remain if persistent hydrolysis is to be avoided. Mixed solvents work by allowing dissolution of hydrophobic moieties in aqueous media but the organic solvents should evaporate to deposit the resin. The distribution coefficients logP (octanol/water) illustrate the hydrophobic character of the solvents used in this study: the values are −0.32 for ethanol, −0.24 for acetone and +0.4 for t-butanol [42]. Thus, in our series, ethanol is the least hydrophobic and t-butanol the most hydrophobic cosolvent found. Tert-butanol also has the highest boiling point (85 °C) compared to acetone (56 °C) or ethanol (78 °C) and will evaporate more slowly. The viscosity of butanol (3.6 cP) is much higher than that of ethanol (1.2 cP) or acetone (0.3 cP) or even water (1.0 cP). On addition of alcohols to water, viscosity increases are observed

[43]. Acetone, or even ethanol, may evaporate too quickly [44] to transport all the hydrophobic monomers to the demineralized front line. Butanol may be a more sluggish but more effective carrier solvent. Our null hypothesis must be rejected, because differences were observed with time for the adhesives tested. These differences must be attributed to the compositions of the adhesives including their solvent content, and to their mode of action.

The infrared spectroscopy results can be interpreted as indicating some water absorption during the 2 year aging period in humid atmosphere. This causes the loss in the resolution of the CH stretching vibrations near 2950 cm^{-1}. This could also provoke the decrease in the intensity of the phosphate band by the dissolution of some phosphate ions loosened by the initial acid etch. However, in vivo, any free phosphate ions present in the hybrid layer may encounter calcium ions circulating in biological fluids and redeposit insoluble calcium phosphate salts. The small differences found in the thermal analysis results of water contents are related to the water present in both the hybrid layer and the underlying dentin, making the values less pronounced than they appear by infrared spectroscopy more related to surface contents.

5. Conclusions

The acid monomers found in the self-etch adhesives investigated are dissolved in mixed solvents and effectively demineralize and clean the smear layer. The products infiltrate the collagen matrix and partly dissolve the calcium phosphate minerals. Both systems decrease dentin permeability significantly, with lowest permeability observed at three months and satisfactory results also observed over a longer one-year period. Also, Xeno V was found to be statistically different from the other adhesive, with a more stable permeability decrease related to a more hydrophobic co-solvent and product.

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