Review article

A review: Biodegradation of resin—dentin bonds

Masanori Hashimoto*, Futami Nagano, Kazuhiko Endo, Hiroki Ohno

Division of Biomaterials and Bioengineering, School of Dentistry, Health Sciences University of Hokkaido, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido 061-0293, Japan

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1. Introduction

Many resin adhesive systems and types have been developed and marketed in dentistry over the last two decades (Fig. 1). The initial attempts at adhesion of resin concentrated on enamel, the first successful attempts to achieve a micro-mechanical interlocking of resin tag formation with acid...
pretreatment being reported by Buonocore [1]. However, resin bonding to dentin could not be achieved due to its complicated structure involving surface moisture and the collagen network. Nakabayashi et al. reported micromechanical bonding of a functional monomer containing resin system (4-META/MMA-TBB) to collagen fibrils in demineralized dentin in 1982 [2]. Since a smear layer created during tooth preparation has an adverse effect on dentin bonding [3,4] due to weak adhesion to underlying dentin [5], its removal by an acidic agent prior to application of a bonding resin require to gain stronger bond strength. Acid-etching of etch-and-rinse systems (total-etching system) demineralizes the dentin surface to expose a few-micron-thick collagen network providing space for resin infiltration. The following application of a primer and/or adhesive penetrates into the interfibrillar spaces of the collagen web, leading to the formation of a hybrid layer composed of collagen fibrils and adhesive resin (Fig. 2). Wet bonding leaves the dentin surface visibly moist after acid etching. This leads to increased resin infiltration into the exposed collagen network as a result of increasing bond strength [6,7]. However, the degree of dentin surface wetness (i.e. moist, wet or over-wet) greatly affects the bond strength in both the laboratory and clinical situations. The depth of demineralization and completeness of monomer diffusion affect the quality of the hybrid layer. When the former exceeds the latter, a region of naked collagen fibers is left exposed as a bond defect (Fig. 3).

For the first system of self-etching adhesives, an acidic monomer of phenyl-P diffuses through extant smear layers to reach the underlying calcium-rich dentin as a result of formation of a hybrid layer where the smear layer remains in the lower half of the hybrid layer [8,9]. The hybridization occurs among resin, collagen fibrils, and inorganic matter of the smear layer (Fig. 2). Theoretically, there are no demineralized dentin zones in the bond face because of the lack of acid pretreatment [8–10]. This system is attractive to clinicians because it is thought the application step is simple and easy compared with total-etching systems with separate etching and water rinsing step.

Newly marketed one-bottle self-etching systems, have been developed with a view to further simplifying the bonding procedure, combining etching, priming, and bonding steps into one component (Fig. 1). These adhesives can be categorized as a self-etching system.

If the hybridized layer is impermeable to water or various chemical stimuli, it could make dentin stable for long-term clinical use. However, many studies have reported the long-term water storage testing of resin–dentin bonds to measure bond strength [11–23]. Most adhesives had decreased bond
strength to various extents after long-term water storage such as for 6 months or 1 year. All such degradation is accelerated in the presence of water [24,25]. The hydrolytic effect of water on the adhesives itself is of great importance when considering the bond degradation. Although the extent of the bond strength reduction is similar for all types of adhesives after aging, micromorphological examination is able to demonstrate the various degradation phases for each adhesive system in in vivo and in vitro. Since the bond structure of the resin—dentin bond depends on the type of adhesive, micromorphological analysis reveals various degradation patterns of bonds after aging.

The objective of this article is to provide a critical review of the degradation of resin—dentin bonds for all types of adhesive systems.

2. Bond degradation of total-etch (etch-and-rinse) adhesives

Acidic solutions (i.e., 35% phosphoric acid) are used to demineralize the smear layer and the underlying intact dentin to expose the collagen network. The incomplete impregnation of the exposed collagen space by subsequent application of bonding resin is due to imperfect resin monomer infiltration (Fig. 3). The discrepancy between the depth of the collagen layer and resin infiltration creates an exposed demineralized dentin zone under the hybrid layer (Fig. 3) [26—35]. These zones correspond with the sites of different modes of silver nitrate staining within the hybrid layer. Spencer and Wang reported resin monomer distribution in the demineralized dentin zone, especially evaluating the heterogeneity of the monomer—collagen interaction, using micro-Raman spectroscopy [34,35]. In their publications, the differentiation of resin monomer diffusion was reveal to depend on the molecular weight of the monomer at the collagen network of the hybrid layer [34,35]. Using atomic force microscopy (AFM), Marshall et al. observed in situ collagen morphology before and after dentin surface treatment [36—38]. The zone of demineralized dentin and the degradation phase were found morphologically using AFM analysis [29]. The exposed collagen fibrils here underwent structural deterioration due to hydrolytic degradation, resulting in decreasing bond strength [12,14—16]. In vivo morphological evidence of collagen hydrolysis was first obtained using extracted human primary teeth with resin restorations [12,39]. Fig. 4 shows collagen degradation within the demineralized dentin in the fractured surface of a resin—dentin bonded specimen (Scotchbond Multi-Purpose) that functioned in human oral environment for 10 months (Fig. 4b). Although an intact hybrid layer is visible in the control specimen at 24 h after bonding (Fig. 4a), hydrolytic degradation of collagen fibrils (Fig. 4b) is clearly observed after aging. There are many lateral branches of dentinal tubules at the fractured surfaces of the dentin side of a specimen in the aged specimen (Fig. 4b), whereas there are none in the control (Fig. 4a). The peritubular matrix of the dentinal tubules is richer in inorganic compounds than the lateral branches and the lateral branches are readily widened by collagen hydrolysis [12,39]. The degradation of the collagen suggests that the resin—dentin bonds made with this adhesive system remained a demineralized dentin zone due to the incomplete encapsulation of the dentin by the resin. The same degrada-

![Figure 4](image-url)

**Figure 4** Scanning electron micrographs of fractured surface of resin—dentin bonded beams. A three-step total-etch adhesive were used for both specimens. Fractured surface were obtained in the dentin side of specimen after microtensile bond test. A fractured surface of control specimens (after 24 h of bonding) (a) and that had been functioning in human oral cavity for 10 months (b). The presence of lateral branches of dentinal tubules is morphological symptom of collagen depletion.

Several in vitro studies using morphological analysis have shown hydrolytic degradation of the collagen mesh in the resin—dentin interface in specimens stored in water for over 1 year [29,39,40]. Transmission electron microscopic examinations have shown the deformation of less stainable collagen fibrils as an indicator of collagen chemical degradation [16,41]. This hydrolysis of collagen greatly affects the long-term bond stability of total-etch adhesive systems. One reason for this collagen hydrolysis may be the effects of saliva or oral bacteria [42,43] in the human oral environment. However, little information is available on the mechanism of collagen degradation in vitro.

Recently, Pashley et al. established a different concept, degradation of naked collagen fibrils by host-derived matrix metalloproteinases (MMPs) in the dentin matrix [44—50]. Matrix metalloproteinases are a family of zinc-dependent proteolytic enzymes that are capable of degrading the organic dentin matrix after demineralization [51]. Although collagenolytic or gelatinolytic activity identified from oral
bacteria [52] may contribute to the hydrolysis of organic matter of the dentinal matrices in the caries process, recent studies have reported host-derived proteinases in the form of different types of MMPs present and released from the dentin matrix [51,53,54]. When a region of naked collagen remains in the demineralized dentin zone, the gradual and slow release of active MMPs dissolves the collagen during the long-term, even in in vitro conditions. In addition, by SEM and TEM micromorphological evidence of self-destruction of collagen has been found in the human dentin matrix in vivo and in vitro [44—50]. Eolation of resin from hybrid layers due to hydrolysis of the resin is a further possible explanation for the bond degradation of total-etching adhesives [17,55—58]. This degradation phase has been found in all type of adhesive systems.

3. Bond degradation of self-etching adhesives

The combination of an etchant and primer into a self-etching primer is advantageous in that it eliminates one application step. For etch-and-rinse systems, factors affecting sensitivity include the surface wetness of the acid etched dentin, acid-etching time, light irradiation time, thickness of the bonding resin layer, consecutive coating methods, and the method of air blowing for the adhesive-coated dentin surface, etc. [6,7,59—61]. For self-etching adhesives, the surface wetness of acid-etched dentin can be theoretically eliminated because there is no water rinsing or dentin moisture retention. The fewer application steps of self-etching adhesives are thought to require less skill by the operator and be easier to implement.

Self-etching primer adhesives differ from the etch-and-rinse systems in that the self-etching adhesives partially involve original smear layers in the hybrid layer [8,9]. The acidic monomer penetrates into the smear layer, smear plug or underlying intact dentin but can be neutralized to stop the demineralization reaction due to pH change [62]. Therefore, the hybrid layer of self-etching systems is a combined structure of resin, collagen fibrils, and minerals. The strong acid of etch-and-rinse systems (i.e., 35—40% phosphoric acid) completely dissolves the matrix of the dentin surface, including the smear layer, exposing the collagen network approximately 3—7 μm in depth. For self-etching adhesives, the smear layer is completely or partially enveloped into the bond structure, providing simultaneous demineralization and infiltration during the application of the acidic monomer, resulting in formation of a hybrid layer. The market-driven simplification of adhesive systems of self-etching primers that combine the conditioning and priming is thought to have overcome the shortcomings of the formation of an exposed collagen network within the bonds of the total-etching adhesives. However, incomplete infiltration was also found as nanoleakage within the hybrid layer [63,64]. Therefore, there is a route for water impregnation into bond faces of self-etching systems after bonding.

One of the beneficial characteristics of a microtensile bond test is that the bond strength measurement can be done for specimens with small adhesive areas (i.e., 1 mm²). Using a microtensile bond test, Sano et al. measured resin—dentin bond strengths in in vivo specimens after long-term function in monkeys [11]. This small adhesive area of the microtensile bond test allowed them to make specimen beams from resin—dentin bonded teeth that had functioned orally. The study revealed evidence of hydrolysis of bonding resin within the hybrid layer of a self-etching adhesive after 1 year of functioning. Later, similar morphological evidence of degradation was confirmed by in vitro tests [13,14]. However, hydrolysis of collagen fibrils is not common as a degradation phase with self-etching adhesive systems. Regions of incomplete resin infiltration or incomplete resin polymerization within the hybrid layer or bonding resin termed nanoleakage have been shown by silver tracer deposition. Although nanoleakage can theoretically be eliminated by using self-etching adhesives, many studies have shown that all self-etching adhesives had a spot- or reticular-mode of nanoleakage within the hybrid layer [63—67]. Although a naked collagen zone was absent within the interface of the self-etching adhesives, it is possible that a loss of resin may initiate and promote proteolytic hydrolysis of collagen. However, this aging pattern is uncommon and which of the structures (collagen or resin) contributes to the bond degradation is unclear. According to the results of these previous studies, resin hydrolysis may be more damaging to long-term bonding effectiveness than collagen hydrolysis in the case of the hybrid layer of self-etching adhesives.

4. Bond degradation of one-bottle self-etching adhesives

Recently, one-bottle self-etching adhesive systems are widely used in clinics because of their simple and easy application. Self-etching adhesive systems are currently available as two-step and single-step types. The single-step self-etching systems can be further divided into two types, the all-in-one and one-bottle types, depending on whether they require mixing or not. The recently introduced all-in-one adhesives are supplied as two-bottles that are mixed together immediately before use. One-bottle self-etching adhesives that combine the etchant, primer, and bonding resin into one bottle with single-step application have been developed, allowing simultaneous etching and priming with one adhesive component. One drop of the adhesive is applied to the dentin/enamel surface with the smear layer covered, resulting in the combination of resin, collagen, and hard tissue as a bonding substrate. This system is generally thought to be less technique-sensitive and time-consuming than traditional adhesive resins (two-step self-etching and etch-and-rinse adhesives). This system is thus attractive for clinicians because of its easy handling and short application time.

Nanoleakage was first visualized in SEM interfacial observations in 1995 [68] and a water tree was first found as an indicator of a leakage pathway by TEM analysis in 2003 [63]. Several studies have shown unfavorable bond defects such as nanoleakage, water trees, bubbles, and phase separation in the bond faces of all-in-one and one-bottle adhesives due to their characteristically high amounts of water [69,70], which is needed for demineralization of dentinal hard tissue by the acid-effect of the monomers of self-etching systems. The hydrophilic nature of bonding resins easily induces water absorption as a result of replacement of the hydrophilic resin monomers even after curing, leading to hydrolytic degradation in the long term [71—77]. Several studies have shown an
increased amount of silver staining in the hybrid layer or bonding resin layer as a function of time using total-etch and self-etching adhesives [78,79]. Recent studies have shown water sorption of adhesive resin to be proportional to the hydrophilic characteristics of the resin [71—79]. The self-etching ability is commonly achieved by incorporation of water in resin monomers that enables ionization of acidic monomers. In addition to the water in the compounds, the ionizable moieties of acidic monomers are also hydrophilic [80]. The presence of such a hydrophilic layer may thus induce water sorption and uptake, in turn, plasticizing the polymer network [17,55—58]. Phase separation of the adhesive or micro-size bubble formation in the bonding resin layer is a typical morphology in one-bottle self-etching adhesive systems [69,70]. A recent study has shown the effect of dentinal surface wetness before bonding on the bond strengths of one-bottle adhesives [81]. In that study, the bonding strengths of resins to dentin were measured using two different surface wetnesses for the dentin substrate before bonding, wet-dentin with short air blowing and dentin dried in a desiccator for 24 h. The hydrophilic one-bottle adhesives with high contents of solvents and water exhibit high water sorption. This water sorption further contributes to a large decrease in the bond strength in wet-dentin compared to dry bonding. An interesting finding was that this result indicated the adverse effect of etch-and-rinse systems on surface wetness. Fig. 5 shows nanoleakage expression (silver staining) in a two-step self-etching specimen (Fig. 5a) and one-bottle self-etching adhesives (Fig. 5b and c) using the back-scatter electron mode of SEM. Although silver staining was observed in the bonding resin layer of one-bottle self-etching adhesives, there is no silver tracer present in the bonding resin when using two-step self-etching adhesives, as shown in Fig. 5a. Based on this, it may be concluded that the nanoleakage expression in bonding resin layers is a special characteristic of one-bottle self-etching adhesives (Fig. 5b and c).

Recently, a typical type of degradation of one-bottle self-etching adhesives was found at the border between adhesives and the resin composite border [82,83]. Although, there was little or no silver staining after 24 h (not shown) of bonding in one-bottle self-etching adhesive specimens, silver particles were present around filler particles of the resin composite between the bonding resin and resin composite border after more than 300 days (Fig. 6) in water. Fractured surface observations also showed a similar degradation pattern (detached filler particles and gap formation) at the same region (adhesive/composite border) in in vitro tests using one-bottle adhesives, despite the fact that similar morphology cannot be found in other adhesive systems [82,83]. A schematic illustration of the region of typical degradation at the adhesive/composite border is shown in Fig. 7. Oxygen inhibits free radical polymerization and yields a thin unpolymerized and/or hydrogel layer on cured surfaces [84—86]. Large amounts of water and/or solvent are responsible for a decrease in viscosity, and lead to oxygen transport to the top surface of the cured adhesive layer, and the depth of the uncured layer with one-bottle adhesives may be more severe than for hydrophobic adhesives. Furthermore, the remaining monomer around the filler around inadequately polymerized monomers will become a pathway for environmental water invasion and entry into the bulk polymer, leading to hydrolysis of the filler-adhesive junction after aging. This poorly polymerized hydrophilic polymer domain is deteriorated rapidly by environmental water and thus is sensitive to interfacial attack by water.
have compatible components from the chemical polymerisation of new adhesive resin systems that are more stable and will open the way for the development of bond degradation.

However, laboratory studies of bond degradation will open the way for the development of new adhesive resin systems that are more stable and have compatible components from the chemical polymer aspect [89–91] and morphological nature in the future. Degradation of the resin composite at the filler–matrix junction (hydrolysis of the silane coupling agent) was easily observed in teeth that functioned in vivo in monkeys and in humans over 1 year [11, 12], though the same morphological results are not available for in vitro aging tests such as long-term water storage or thermal cycling. Many studies have reported the enzyme-catalyzed hydrolysis of ester linkage in methacrylate-based monomers of resin composite [43, 92–94]. It is well known that esterases (i.e., cholesterol esterases, salivary esterases, or porcine liver esterases) induce ester hydrolysis. In contrast to resin or collagen hydrolysis, careful comparison between in vivo and in vitro resin composite degradation is needed. In addition, analysis of the degradation of bonding resin by esterases in vitro will be an important research topic in the future.

A variety of chemical and physiological factors affect the durability of resin–dentin bonds. This review article concentrates on the morphological evidence of bond degradation. The long-term durability and degradation patterns of resin adhesives have changed with the types of adhesives during the last two decades. There are clear differences among total-etching systems (etch-and-rinse system), self-etching system, and one-bottle self-etching systems. Typical morphological evidence of degradations is provided by collagen hydrolysis of total-etch adhesive systems, resin elution from the hybrid layers of all systems, and hydrolytic degradation at the border between the adhesive/composite junction of one-bottle self-etching adhesives. In addition, the results in many previous studies give promise for the translation of in vitro into in vivo results for bond testing and morphological analysis of resin and collagen hydrolysis. This biodegradation research will provide an avenue of progress for newly developed resin adhesives.

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