Review Article

The Generations of Enamel-Dentin Bonding Agents: An Update

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ABSTRACT

Adhesive dentistry has a revolution in restorative dental practice during the past 50 years. Contemporary restorations are replaced by adhesive materials completely. Improved resin-based composite restorations are more reliable and long-standing. In addition, techniques are more conservative which depends less on mechanical retention and removal of un-supported enamel. The purpose of the article is to offer a concise, comprehensive, and an update on seventh-generation bonding agent. Moreover, the dental bonding agents evolved from total-etch (fourth- and fifth-generation) to the more recent self-etch systems (sixth- and seventh-generation). The present article is based on the review of literature and companies researches.

Key words: All-in-one, Enamel and dentin bond strength, Hybrid layer, Self-etch, Seventh generation, Smear layer

INTRODUCTION

Buonocore (1955) research said that etching enamel increased the duration of adhesion under water. The technique had been inspired by industrial phosphoric acid bonding system and used as a surface treatment before the application of the resins.[1] He demonstrated his insight into adhesion dentistry and suggested the formation of resin tags that caused the principal adhesion of the resins in the microporosities of acid-etched enamel.[2-4] The present article is an update on bonding agents and highlighted the seventh-generation bonding agents. The update is based over the manufacturer researches and scientific publications. Fusayama *et al.* (1979) used 37% phosphoric acid for 60 s to etch enamel and dentin. This study demonstrated that procedure did not increase pulp damage and improved the adhesion to enamel and dentin. These were called as third-generation adhesive.[5]

The tooth bonding procedure involves the application of a bonding agent before the filling of a resin composite. In addition, early dentin bonding was complicated by the presence of the smear layer [Figure 1]. A previous study on dentinal walls has been performed by Brannstrom and Johnson (1974) after cavity preparation that showed the presence of a thin layer of debris of 2–5 micrometers thick.[6] Smear layer is the organic debris that remains on the dentin surface after the preparation of the dentin during restoration of a tooth. The smear layer blocks the dentinal tubules completely and acts as a "diffusion barrier."

Nakabayashi and Pashley highlighted the formation of the hybrid layer between the etched dentin and adhesive material.[7,8] Hybrid layer consisted of collagen network exposed with etching and embedded in adhesive resin [Figure 2]. These binding agents belong to the fourth generation. A light activated compound added in the adhesive resin. Primer and adhesive resin are cured simultaneously for the minimum time.[9,10] The layer thickness of bonding agents was at least 50 μm to prevent the diffusion of oxygen from atmosphere between the primer and bonding adhesive during polymerization.

In fifth-generation, one-bottle systems evolved to facilitate the clinical use. It combined the primer and adhesives into one solution. Bonding applied after etching the enamel and dentin simultaneously (the total-etch wet-bonding technique) with 35–37% phosphoric acid for 15–20 s.[11] Watanabe and Nakabayashi developed a self-etching primer that was an aqueous solution of 20% phenyl-P in 30% HEMA for bonding to enamel and dentin simultaneously.[12]

The bonding agents should be biocompatible, non- toxic, non-irritant, and non-poisonous. They also have low film thickness, low viscosity form, strong permanent bond, and good dimensional stability. It should have low thermal conductivity, good shelf life, and prevent micro leakage. The contemporary journey of bonding system started from first generation and travels to seventh generation since 1955–2013[13] [Table 1]. Dental bonding systems come in three forms. First is three-step system – the etchant, primer, and adhesive. Second is two-step system, the etchant and the primer are combined with adhesive. Third is one-step system, all the components premixed and applied in a single application which is known as seventh generation of bonding agent.[14] Bonding agents were classified according to numbers of steps of

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Table 1: Chronological evolution of seventh-generation bonding agents

S. No.	Generation	Evolution	Development
1	First generation	1950–1970	Etchant was 37% phosphoric acid. Development of surface active monomer NPG-GMA. It chelates the calcium from tooth surface and forms weak bonds. Bond strength is low, that is, 1–3 MPa
2	Second generation	In the late 1970s	Esters of unfilled resins such as bisphenol-A glycidyl methacrylate (bis-GMA) and hydroxyethyl methacrylate (HEMA) in ethanol. Draw back was weak bond 5–6 Mpa, loosely attached smear layer and hydrophobic in nature
3	Third generation	Mid to late 1980s	Partially removes and/or modifies the smear layer. Primer is 4-META and biphenyl dimethacrylate (BPDM). Adhesive is unfilled resin in HEMA. Bond strength is weak 5–8 MPa
4	Fourth generation	Early 1990s	Smear layer is removed. Total-etch bonding technique. Etching is done and A hybrid layer was formed from the primer- polymerized methacrylate on moist dentin. Then adhesive is applied. A light activated compound is added in the adhesive resin. Bond is strong as 13–30 MPa
5	Fifth generation	Mid to late 1990s	One-bottle systems combined either conditioner with primer or the primer with adhesives into one solution. Bond is 13–25 Mpa
6	Sixth generation	Early 2000s	Smear layer is modified to form the hybrid layer and less post-operative sensitivity. Two step and one step (self-etch is available. ACIDIC PRIMER Adhesive: - Methacrylated phosphates SOLVENT:- Water. Bond is inferior to fifth and forth generation
7	Seventh generation	Mid 2005	Self-etch-one bottle is an acetone/water-based formulation of light-activated methylacrylate resins
8	Eight generation	Near 2010	Dual cure self-etch – self-cure and light cure

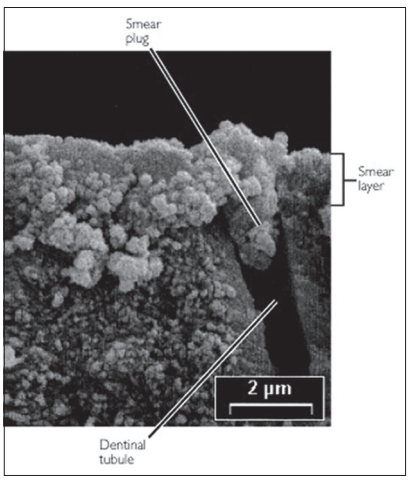

Figure 1: Scanning electron micrograph of the fractured edge of smear layer-covered by human dentin. Note the presence of smear plugs occluding the orifices of the tubules

application [Table 2]. The aim of present article is to discuss in brief the updated classification of bonding agents. The current product, seventh generation and self-etch – all-in-one is highlighted to improve its clinical use and performance.

BONDING AGENT OF SEVENTH GENERATION

It combines etchants/conditioners, primers, and adhesives in one bottle[15] and the key components of bonding system are discussed and disclosed altogether in [Table 3]. These materials involve only a single step which eliminates separate etching, rinsing, and

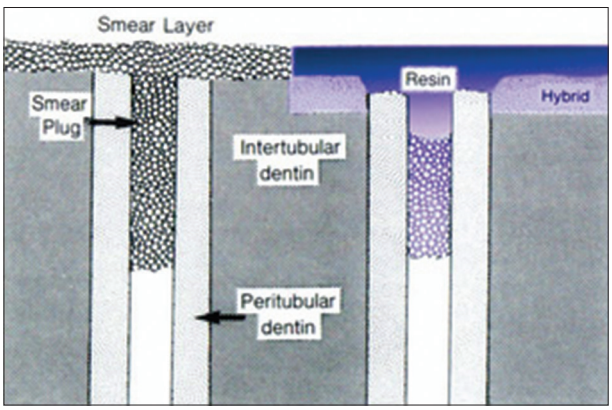

Figure 2: Schematic illustration of the self-etching primer adhesive systems. The self-etching primer (violet) and adhesive (purple)

mixing for the light-cured products. The self-etching seventh-generation bonding agents used acidic monomers that etch prime dentin. These monomers are also able to the etch cut enamel, but some may not be enough strong to adequately etch uncut enamel. Phosphoric acid is a better etchant of uncut enamel. The tensile bond strengths to enamel and superficial dentin are typically greater than that to deep dentin as follows.

Ground enamel	Deep dentin	Superficial dentin
20 MPa	18 MPa	25 MPa

Ideal features of a seventh-generation bonding agent:

- High bond strength to enamel and dentin [Table 4]
- Thin film thickness to ensure complete seating of restorations
- Fluoride-releasing to prevent onset of secondary caries

- Delivery option – only one bottle or unit-dose
- Tolerant to moist and dry environment
- Radiopaque and easier to differentiate adhesive layer from recurrent caries
- Little to no margin discoloration over time

Table 2: Classification based on steps of application

Generation	Steps	Description
First	3	Etch enamel and dentin, apply primer, and adhesive
2nd	3	Etch enamel and dentin, apply primer, and adhesive
3rd	3	Etch enamel and dentin, apply primer, and adhesive
4th	3	Total-etch, apply primer, and adhesive
5th	2	Total-etch, apply primer+adhesive
6th	1 or 2	Self-etch, all-in-one or total-etch, apply primer+adhesive
7th	1	Self-etch, all-in-one
8th	1	Dual cure – self-cure and self-etch – all-in-one

Table 3: Composition of seventh-generation bonding agents: self-etch-one bottle

1	Etchant/conditioner; cleans and demineralizes the enamel and dentin. Acid monomer (Phosphoric Ester Monomer – 1–5%) self-etches works as conditioner
2	Primer: a hydrophilic, low viscosity resin that promotes wetting and bonding to enamel and dentin. They are carried in acetone, ethanol, and water (50–70%). 4 META-10–15%: 4 Methacryloxyethyl trimellitate anhydride works as primers
4	Adhesive: it promotes bonding among the enamel, dentin, restorative material, and cements. Mostly hydrophobic monomer of urethane dimethacrylate (5–9%) and dimethacrylate component (8–12%) are used Photo initiator: light activated product – typically camphorquinone with organic amine
6	Filler: control handling, improve strength and increases the thickness layer of adhesive. Submicron glass particles and nanofillers act as fillers
7	Others ingredients: fluorides, desensitizers, calcium salts, and antimicrobial ingredients

- Available in light-cured and dual-cured formulations
- Low hypersensitivity – it can be used in place of liners and bases in deep cavities.[16]

The 8th generation bonding agent is compatible with total-etch, self-etch, and selective etch techniques. It provides excellent versatility and perfectly adapts to all direct restorations and can also be used to repair indirect restorations without the use of a primer, and also in combination with a silane when repairing glass or hybrid ceramic and is also ideal for hypersensitivity.

A unique combination of three functional monomers (4-MET, MDP, and MDTP), notably excluding HEMA, confirms its excellent stability and good bond strengths not just to tooth tissue but to all indirect substrates, including composites, precious and non-precious metals, zirconia, and alumina for all repair cases.

The 8th generation bonding agent is applied to tooth structure using a micro brush and left undisturbed for 10 seconds. after application, followed by thoroughly air drying for 5 seconds under maximum air pressure and light-cured for 10 seconds.[17]

DISCUSSION

Seventh-generation bonding agents utilize the smear layer as a bonding substrate.[17] The acidic primer demineralizes the smear layer and the top layer of the underlying dentin surface. The acidic primer also infiltrates the exposed collagen, along with the hydrophilic monomers which then copolymerize, because the etched surface is not rinsed; the demineralized smear layer is incorporated into the hybrid layer. The hybrid layer ranges in thickness from 0.5 um to 5 um. The acidic primer (4 META) and adhesive monomers (Dimethylacrylate component) also infiltrate into the collagen fibers as the primer decalcifies the inorganic component in dentin to the same depth, which should minimize voids, potential leakage, and post-operative sensitivity. This mechanism also minimizes the hypersensitivity. With the total-etch systems, phosphoric acid is used to demineralize the dentin. In a separate step, a primer is applied over the demineralized dentin. Hence, there is potential

Table 4: Bond strength of seventh-generation self-etch adhesive system

Product	Company	Packing	Bond strength enamel (Mpa)	Bond strength Dentin (Mpa)
AdapterTMEasy bond	3M ESPE St. Paul, MN	Single bottle, unit dose	23	28
AdheSeTM One	Ivoclar vivadent, Inc Amherst, NY	Single bottle	19	23
Clearfil* S3 Bond	kuraway America, Inc New York, NY	Single bottle, unit dose	32	28
G-BondTM	GC America. Inc Alsip, IL	Single bottle, unit dose	20	20
I- BondTM Self-Etch	Heraeus Kulger GmbH, 63450 hanau	Single bottle, unit dose	26	29
OptiBond* All-in-one	Kerr corp orange, CA	Single bottle, unit dose	28	28
Xeno* IV	Dentsply caulk Miford DE	Single bottle, unit dose	21	25
Dual cure system				
Clearfil* DC Bond	kuraway America, Inc New York, NY	Single dose	19	nt*
Xeno* IV Dual cure	Dentsply caulk Miford DE	Bottle, unit dose (except activator)	25	18

nt*: Not tested

for a layer of weak demineralized dentin below the dentin that has been penetrated by the primer. This layer of wet, collapsed collagen, can potentially cause a weak adhesive layer that causing microleakage.

Most of the seventh-generation bonding agents have water as a solvent. The sensitivity is also reduced by the addition of fluoride, salt of calcium, and glutaraldehyde. Consequently, the wetness or dryness of the tooth surface is less critical than it is with bonding agents as with solvents containing ethanol or acetone. *In vitro* researches, on contaminated tooth substrates with human saliva or human blood showed that bonding agents based on acidic primers, to be less sensitive to these contaminants. It is recommended that heavily contaminated tooth surfaces be rinsed with water and then bonding agent could be reapplied. Draw backs of this category bonding agent are short shelf life due to acid formulation; therefore, it needs refrigeration. Self-etch system is also not compatible with dual cured composite cores and resin cements due to dual cure bonding agents are recommended for them.

The shear bond strength of 7th and 8th generation self-etch dentin bonding agent on pediatric teeth is evaluated and compared and result of Mishra *et al*., in 2020, showed that eighth-generation bonding agent has better shear bond strength than seventh generation.[18]

CONCLUSION

Present era of restorative dentistry is based over the resin base composite restorations. Obviously, Dentin bonding agents have evolved from no-etch to total-etch to self-etch systems. The development of self-etching primer adhesive systems has greatly simplified resin bonding procedures as a separate etching step is no longer required. These self-etching primer adhesives can be used simultaneously to etch and bond both the enamel and dentin entirely. It bonds equally well to superficial and deep dentin. Bonding agent could be used in place of liners and bases in deep cavities if they are covered with an intermediary resin composite. Seventh-generation bonding agents offer good bond strengths to tooth structure and less technique sensitivity than etch-and-rinse (total-etch) and sixth-generation bonding agents. Author suggested that it might be excellent choices of the bonding agent for the direct, indirect resin, and all-ceramic posterior restorations.

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