Dentin Bonding Unveiled: A Look at the Past, Present, and Future Innovations

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Abstract

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Dentin bonding agents are designed to enhance the clinical effectiveness and longevity of resin-based restorations. Despite advancements in adhesive systems, the bonded interface remains the most vulnerable aspect of tooth-colored restorations. Earlier adhesives were prone to failures due to loss of retention and inadequate marginal adaptation. However, the advent of reliable adhesive materials has minimized the need for extensive tooth preparation, promoting a more conservative approach. Dentin bonding has undergone significant evolution, transitioning from no-etch to total-etch and self-etch systems. The introduction of self-etch primer adhesives has streamlined bonding procedures by eliminating the need for a separate etching step. Modern dental bonding systems are categorized as three-step systems (sequential application of etchant, primer, and adhesive), two-step systems (combined etchant and primer), and one-step systems (pre-mixed components applied in a single step), often referred to as seventh-generation bonding agents. This article delves into the mechanisms, advancements, and newer generations of bonding agents, including self-etch and total-etch systems, with a focus on their role in achieving durable and effective adhesive restorations.

Keywords: Dentin bonding agents, Hybrid layer, Enamel adhesion, Self-etch adhesives, Adhesive dentistry advances, Smear layer

INTRODUCTION

Minimally invasive dentistry has replaced the traditional "drill and fill" approach, prioritizing the preservation of healthy tissue over artificial replacements. Adhesive materials have revolutionized clinical practice by enabling conservative cavity preparations and favoring repair over complete restoration replacement.[1,2]

Despite advancements, secondary caries at gingival margins, primarily due to unreliable dentin bonding, remain the leading cause of failure in moderate to large composite restorations. While enamel bonding is reliable, achieving a durable dentin bond remains challenging, with the resin-dentin interface often being the weakest link. Modern adhesive systems have improved retention, but robust dentin bonding continues to require innovation.[3]

Over the past four decades, advancements in adhesive monomers and dentin pre-treatment have enhanced dental adhesive technology, significantly improving restorative outcomes. This progress has shifted cavity preparation from G.V. Black's extension for prevention to a lesion-centered approach. Innovations in adhesive materials, caries detection, magnification, digital radiography, and risk assessment now support more conservative and effective caries management.

History of Dentin Bonding Agents

In the early 1950s, research into materials capable of bonding resins to tooth structures began. The first notable development in adhesive dentistry was achieved by Dr. Oskar Hagger, a Swiss chemist working for DeTrey/Amalgamated Dental Company. In 1951, he introduced the first dental adhesive product, "Sevriton Cavity Seal," which utilized glycerophosphoric acid dimethacrylate (GPDM) as its adhesive component. [4]

In 1952, a study by McLean and Kramer highlighted the potential of "Sevriton Cavity Seal," noting that GPDM improved dentin adhesion by penetrating the surface and forming an intermediate layer.[5] **Buonocore et al (1955)** conducted experiments to enhance the adhesion of acrylic filling materials to enamel surfaces, a major limitation in restorative dentistry at the time. It was concluded that in intraoral tests, the treated surfaces exhibited significantly improved adhesion compared to untreated controls. This marked an early step toward understanding resin-to-tooth bonding mechanisms.[6]

The field took a revolutionary turn in 1955 with the work of Dr. Michael Buonocore, widely regarded as the pioneer of adhesive dentistry. Inspired by techniques used in the automotive industry, where phosphoric acid was applied to metal surfaces to enhance primer adhesion, Buonocore introduced the concept of acid-etching to dentistry. He demonstrated that treating enamel surfaces with phosphoric acid significantly improved resin adhesion. In his landmark research, Buonocore used 85% phosphoric acid, setting the foundation for modern adhesive dentistry. [7]

Classification of Dentin Bonding Agents

1. **By Generations**: [8-11]

A tabulated difference comparison between the various generations has been described in the Table no. 1

Generation	Key Characteristics	Composition	Mechanism of Action	Limitations
First Generation e.g., Cervident	Initial adhesive dentistry systems	Glycerophosphoric acid dimethacrylate (NPG-GMA)	Micromechanical retention; ionic and covalent bonding	High polymerization shrinkage, high thermal expansion, poor durability, sensitive to water

Second Generation e.g., ScotchBond	Introduction of hybrid layer	Polymerizable phosphates, bis-GMA resins	Micromechanical and chemical adhesion; ionic bonds	Weaker bond due to smear layer, prone to degradation in water
Third Generation	Etch-and-rinse technique introduced	Hydrophilic and hydrophobic monomers	Micromechanical retention and chemical bonding	Weak link with unfilled resins, sensitivity in etching dentin
Fourth Generation eg: Optibond FL	Total-etch technique, gold standard	Advanced adhesive monomers, hydrophilic and hydrophobic monomers	Micromechanical interlock and chemical bond	Technique-sensitive, multiple steps, complex application
Fifth Generation E.g., Adper Single Bond 2(3M, ESPE)	Simplified application, one-bottle system	Combined primer and adhesive, advanced monomers	Micromechanical retention and chemical bonding	More susceptible to water degradation, not always compatible with dual/self-cured materials
Sixth Generation e.g., Clearfil SE Bond, (Kuraray dental	Self-etch systems, reduced steps	Acidic monomer for conditioning and priming	One-step self-etch, no rinsing	
Seventh Generation e.g., iBond (kerr).	Single-step, self-etch systems	Combined conditioner, primer, bonding resin	No separate etching step	High water content, prone to hydrolysis, limited long-term data
Eighth Generation e.g., Scotchbond Universal Plus (3M ESPE)	Incorporation of nanosized fillers	Polyfunctional adhesive monomers, SiO_2 nanoparticles	Improved resin penetration, thicker hybrid layer	High viscosity with larger nano-fillers, potential for flaws

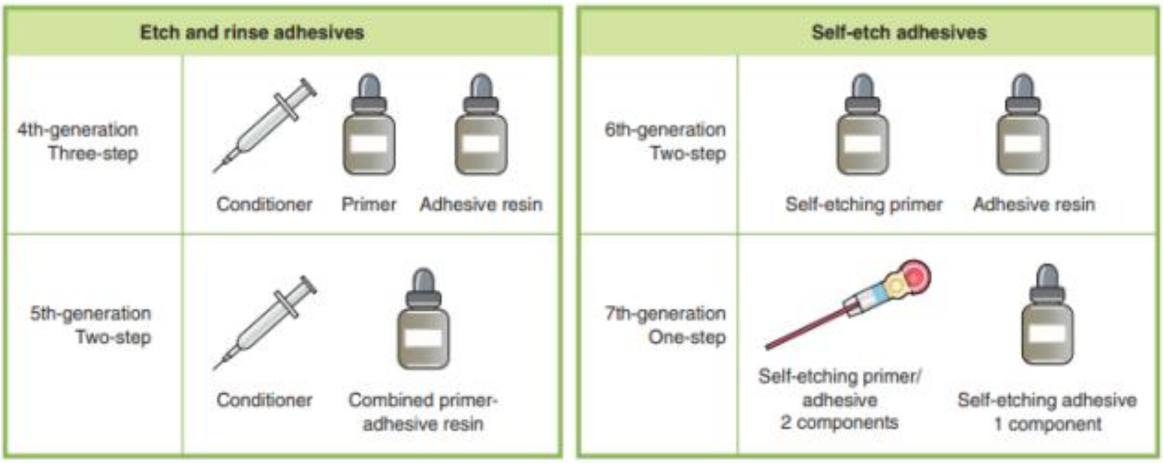

Figure 2: Classification of current adhesive systems according to van Meerbeek et al. 2003. (Figure adapted from Cardoso MV, de Almeida Neves A, Mine A, et al: Current aspects on bonding effectiveness and stability in adhesive dentistry. Aust Dent J 56(S1):31–44, 2011.) [12]

2. **By Procedural Steps**:[13]
- Three-step systems (etching, priming, bonding) e.g., Scotchbond Multipurpose (3M ESPE)
- One-step self-etch adhesives e.g., Xeno V (Dentsply Sirona).

Hanabusa et al (2012)[14] evaluated if a new one-step adhesive could be applied in a multi-mode manner, either 'full' or 'selective', self-etch and etch-and-rinse approaches and concluded that the bonding effectiveness of the one-step self-etch adhesive could be improved by etching the enamel margins selectively with phosphoric acid.

3. **By Etching Pattern**:[15]
- Total-etch systems (fourth and fifth generations) e.g., Adper Single Bond 2.
- Self-etch systems (sixth and seventh generations) e.g., Scotchbond Universal Plus.

4. **By pH Levels**: [16]
- Strong (pH 1) e.g., Tyrian SPE,
- mild (pH 2) e.g., Clearfil SE Bond,
- intermediate (pH 1.5) e.g., OptiBond All-In-One self-etch adhesives.

Ahn et al (2015)[17] concluded that the effect of additional acid etching on the dentin bond strength was influenced by the pH of one-step self-etch adhesives. Ethanol wetting on etched dentin could create a stronger bonding performance of one-step self-etch adhesives for acid etched dentin.

Composition of Dentin Bonding Agents

Dentin bonding agents consist of various key components. [18]

Following is a detailed table summarizing the composition of dentin bonding agents:

Component	Type	Description	Function
Etchants	Strong Acids	Typically phosphoric acid (30-50%, usually around 37%).	Removes smear layers and dissolves the mineral phase to facilitate micromechanical interlocking.
Primers	Solutions	Contain hydrophilic monomers (e.g., HEMA) dissolved in solvents (water, ethanol, acetone).	Keeps the collagen network expanded, allowing hydrophobic adhesive monomer infiltration.
Adhesives	Resin Compositions	Mainly hydrophobic dimethacrylates (e.g., bis-GMA, TEGDMA, UDMA) with some hydrophilic monomers (HEMA).	Fills the interfibrillar space, creating a hybrid layer and resin tags for micromechanical retention.
Initiators	Chemical Agents	Includes photoinitiators (e.g., camphorquinone), self-cure systems (e.g., benzoyl peroxide), and dual-cure systems.	Initiate the polymerization process of adhesives and restorative composites.
Filler Particles	Nanoparticles	Nanometer-sized silica particles added to some adhesives.	Reinforce adhesives, increase bond strength, and modify viscosity.
Other Ingredients	Additives	Includes glutaraldehyde (desensitizer), MDPB and parabene (antimicrobials), fluoride (prevents caries), and chlorhexidine (prevents collagen degradation).	Enhance effectiveness and longevity of bonding agents.

Patterns of etching: [19]

Type 1	Most common etching pattern. This involves removal of enamel prism cores with prism peripheries remaining leaving intact
Type 2	Here peripheries are removed leaving the cores intact
Type 3	This is associated with the presence of prism less enamel

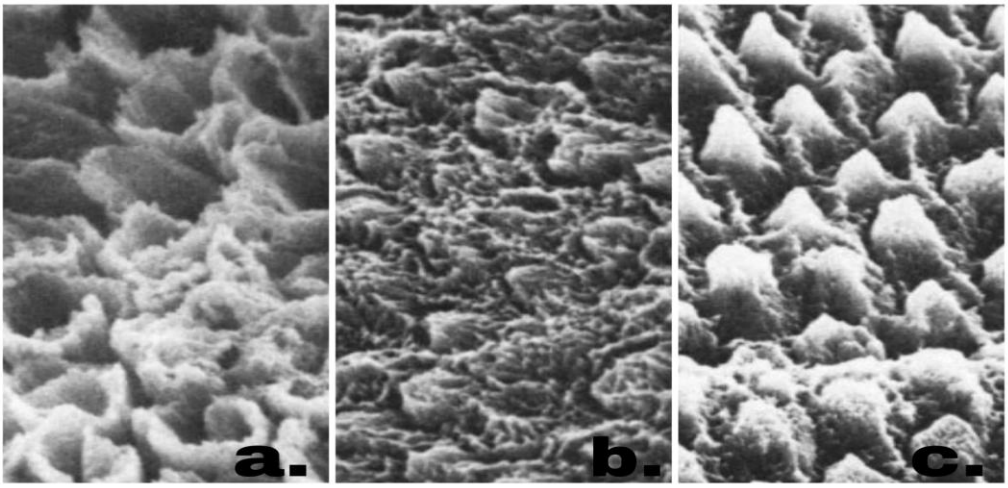

Figure 1. : a. type 1 etching pattern, b. type 2 etching pattern, c. type 3 etching pattern
Source: Galil, K.A. and Wright, G.Z., 1979. Acid etching patterns on buccal surfaces of permanent teeth. Pediatr Dent, 1(4), pp.230-4.

Bonding to Hydroxyapatite: [20]

The formula M-R-X) shows the chemical bonding in dentistry.
M - Stands for the methyl methacrylate group including the -CO-O- bond).
R - stands for a spacer consisting of a hydrocarbon chain,
X - is the group capable of bonding to calcium present on the tooth surface.

The Smear Layer In Dentin Bonding

Pashley et al (1981)[21] observed that the removal of the smear layer allowed for increased fluid filtration across dentin, emphasizing its role as a barrier to convective transport. The smear layer, formed during tooth preparation, consists of dentin debris, hydroxyapatite, and collagen. It blocks dentinal tubules, reducing permeability and adhesive penetration, but can be modified or removed using agents like sodium hypochlorite, EDTA, or phosphoric acid to enhance adhesion and bond strength **(Goldman et al. (1981))**.[22]

The Hybrid Layer in Dentin Bonding

The hybrid layer, first described by **Nakabayashi et al. (1991)**[23], is a resin-dentin interface essential for durable bonding. It consists of demineralized collagen and infiltrated resin, forming a mechanical and chemical bond that enhances resistance to microleakage. However, it is prone to degradation from hydrolysis, incomplete resin infiltration, and enzymatic activity (e.g., MMPs, CTs). Strategies such as cross-linking agents and optimized adhesive formulations help stabilize the hybrid layer. **Frassetto et al (2015)**[24] stated that inhibiting collagenolytic activity and employing cross-linking agents are two primary strategies To enhance the resistance of the hybrid layer to enzymatic degradation.

Enamel and Dentin Adhesion

Enamel adhesion relies on acid etching to create microtags within the enamel, significantly enhancing bond strength, often exceeding 20 MPa. Shorter etching times have proven effective in maintaining bond efficacy while reducing the risk of complications. Dentin adhesion, however, is more complex due to its moisture-sensitive nature. It involves resin infiltration into the collagen network, forming a hybrid layer essential for strong, durable bonds. **Perdigão (2010)** discussed the variables related to clinical situation and substrate treatment in dentin bonding. The author identified crucial factors—wetness of dentin, pulpal pressure, and dentin thickness— influencing bonding procedures. **Malacarne et al (2006)**[25] evaluated the water sorption, solubility and kinetics of water diffusion in commercial and experimental resins that are formulated to be used as dentin bonding agents and concluded that extensive water sorption affected the mechanical stability and lead to potential dentin bond degradation. Proper moisture control and precise etching protocols are critical for optimizing adhesion.

Recent Advances in Dentin Bonding Agents

Recent advancements in adhesive dentistry have focused on improving both performance and longevity. Functional monomers have enhanced hybrid layer stability, while protease inhibitors have been introduced to prevent collagen degradation. ER:YAG lasers have emerged as a valuable tool for removing the smear layer and creating micro-retentive features, improving bond strength. The incorporation of nanoparticles has further reinforced bonding agents, promoting remineralization and enhancing durability. Universal adhesives have simplified the bonding process, with crosslinkers offering additional improvements in performance.[26] **Mahmoud (2023)**[27] discussed the various strategies for improving the performance of dental adhesive systems incorporating anti-MMP and collagen crosslinking agents, bioactive glass for remineralization, and antibacterial agents such as Quaternary Ammonium Salts (QAS), MDPB monomer, and Benzalkonium chloride. Looking ahead, future developments in adhesive dentistry include biomimetic adhesives, self-repairing systems, fluorescent markers for detecting marginal leakage, and the integration of digital technologies for creating custom bonding solutions.

CONCLUSION

Dentin bonding agents have undergone remarkable evolution, transforming restorative dentistry with advancements that address critical challenges like bond strength, durability, and tooth structure preservation. From the early generations focused primarily on enamel bonding to the latest bioactive and biomimetic adhesives, these agents have consistently pushed the boundaries of dental science and clinical efficacy. Looking ahead, the future of dentin bonding agents lies in the exploration of bioactive materials and biomimetic strategies that closely mimic natural tooth structures while promoting remineralization and tissue preservation. As research and technology continue to progress, these cutting-edge adhesives will revolutionize restorative dentistry, ensuring better outcomes for patients and enabling dental professionals to deliver care that is both highly effective and minimally invasive.

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