The Progression of Dental Adhesives

A Peer-Reviewed Publication
Written by Ara Nazarian, DDS

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Educational Objectives
Upon completion of this course, the clinician will be able to do the following:
1. Be knowledgeable about the evolution of bonding adhesives
2. Know the attributes of an ideal bonding agent
3. Be knowledgeable about the properties of the seventh-generation adhesives and the advantages they offer
4. Know the applications that seventh-generation adhesives can be used for and understand the techniques that should be used

Abstract
There has been dramatic progression in the adhesion of dental adhesives and resins to enamel and dentin in the 40 years since Buonocore1 introduced the technique of etching enamel with phosphoric acid to improve adhesion to enamel. The first dental adhesives bonded resins to enamel only, with little or no dentin adhesion. Subsequent generations have dramatically improved bond strength to dentin and the sealing of dentin margins while retaining a strong bond to enamel. With more patients demanding metal-free dentistry, the use of dental resins as cements as well as direct and indirect restorations will continue to increase. This article discusses the progression of dental adhesives up to the most recent generation, in which all components are contained in a single bottle or unit-dose container and applied using a one-step technique that requires no mixing.

Overview
Over the past 45 years, dental bonding systems have evolved with variations in chemistry, application, mechanism, technique, and effectiveness. This evolution accompanied the development of improved esthetic dental materials, notably composite resin and ceramic, and an increasing demand by patients for esthetic dentistry. In 1999, approximately 86 million direct resin restorations were placed. With respect to indirect restorations, approximately 2.5 million veneers, 38 million resin/ceramic crowns, and 1.1 million ceramic/porcelain inlays were placed, in addition to metal-based crowns and bridges and core/post and core build-ups.2 All direct resin restorations require bonding, and indirect restorations either require or are candidates for bonding. As the demand for bonded esthetic restorations has continued to increase, the evolution of bonding agents has accelerated.

History of Bonding Agents
First and Second Generation
The first- and second-generation bonding agents used during the 1960s and 1970s did not recommend etching the dentin, but instead relied on adhesion to the attached smear layer.3 The weak bond strength (2MPa–6MPa) to the smear layer still allowed dentin leakage with clinical margin stain.4

Third Generation
The third-generation systems of the 1980s introduced acid etching of dentin and a separate primer designed to penetrate the dentin tubules as a method to increase bond strength.3 These systems increased bond strength to dentin (12MPa–15MPa) and decreased dentin margin failure. With time, however, margin staining caused clinical failure.4

Fourth Generation
The fourth-generation adhesive systems of the early 1990s used chemistry that penetrated both etched and decalcified dentin tubules and dentin substrate, forming a “hybrid” layer of collagen and resin. Fusayama5 and Nakabayashi6 described the penetration of resin into dentin as giving high bond strengths and a dentin seal. In fact, Kanca7 introduced the idea of “wet bonding” with these systems. Products in this category include All-Bond® 2 (Bisco), OptiBond® FL (Kerr), and Adper™ Scotchbond™ Multipurpose (3M ESPE). These bonding agent systems have the longest track record as far as research goes and they perform well clinically. In fact, OptiBond FL, an 18-year-old product, received the Product of the Year award from Reality magazine.8 Bond strengths for these adhesives were in the low- to mid-20MPa range and significantly reduced margin leakage compared to earlier systems.4 This system was very technique sensitive and required an exacting technique of controlled etching with acid on enamel and dentin, followed by two or more components on both enamel and dentin. Because of the complexity of multiple bottles and steps, dentists began requesting a simplified adhesive system.

Fifth Generation
That request ushered in the fifth-generation bonding systems, introduced during the mid 1990s, which combined primer and adhesive in one bottle while maintaining high bond strengths. Products in this category include Excite (Ivoclar Vivadent), OptiBond® Solo Plus™ (Kerr), Prime and Bond® NT (Dentsply), and Adper™ Singlebond™ (3M ESPE). Unit-dose packaging introduced during this era

All direct resin restorations require bonding
provided fresh chemistry for each procedure. Yet controlled etching, surface wetness, and resin placement continued to be a clinical challenge for some clinicians.

**Sixth Generation**

The sixth-generation bonding systems introduced in the latter part of the 1990s and the early 2000s—also known as the “self-etching primers”—were a dramatic leap forward in technology. The separate acid-etching step was eliminated by incorporating an acidic primer that was placed on the enamel and the dentin after tooth preparation. Several variations involved either mixing the acidic primer and adhesive before placement on the dentin and enamel, or leaving the primer on the tooth and then placing the adhesive over the primer. Some products in this class are Clearfil® SF Bond (Kuraray), Simplicity™ (Apex), Adper™ Prompt™, and L-Pop™ (3M ESPE). These systems were also reported to reduce the incidence of post-treatment sensitivity found in previous systems. However, the bond strength to dentin and enamel is lower than fourth- and fifth-generation systems (Table 1).

**Ideal Bonding Agent Attributes**

Attributes of an ideal bonding agent would include high bond strength, a thin film thickness to ensure easy and complete seating of restorations, shelf stability, and post-placement stability. The ability to release fluoride is desirable to help prevent the onset of secondary caries, which is the leading reason for replacement of existing restorations. In addition, the bonding agent should be user-friendly—ideally a one-step procedure requiring no mixing, with the versatility to be used for multiple types of restorations (indirect and direct, resin/ceramic, and metal), and tolerant of both moist and dry environments (Table 2).

**Table 1. Evolution of Bonding Adhesives**

<table>
<thead>
<tr>
<th>Period</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960s and 1970s First and Second Generation</td>
<td>Did not recommend dentin etching. Relied on adhesion to smear layer. Weak bond strength.</td>
</tr>
<tr>
<td>Mid 1990s Fifth Generation</td>
<td>Combined primer and adhesive in one bottle. Maintained high bond strengths. Unit-dose packaging introduced.</td>
</tr>
<tr>
<td>Late 1990s, Early 2000s Sixth Generation</td>
<td>“Self-etching” primers. Reduced incidence of post-treatment sensitivity. Bond strengths lower than fourth- and fifth-generations.</td>
</tr>
</tbody>
</table>

**Seventh Generation Bonding Systems**

The latest category, seventh-generation bonding systems, is the “all in one” adhesives that combine etch, prime, and bond in a single solution. This adhesive category was introduced in late 2002. Laboratory studies show bond strengths and margin sealing to be equal to sixth-generation systems. Products in this category include iBond™ (Heraeus), Xeno® IV (Dentsply), G-Bond™ (GC), Complete (Cosmedent), and OptiBond® All-In-One (Kerr). Both OptiBond All-
in-One and Xeno IV are fluoride releasing, while iBond and G-Bond are not.

The all-in-one adhesives are user-friendly, and most offer both a bottle and a unit-dose version. There are variations on other attributes depending on the product used. Shear bond strength, a key attribute in dental adhesives, varies considerably depending on the self-etch adhesive used. (Figure 1)

Xeno IV self-etch seventh generation adhesive is available in a bottle or unit dose delivery and does not require mixing. Xeno IV is pH balanced to reduce gingival irritation and sensitivity. Clearfil S3 Bond, G-Bond and iBond are available in a bottle. Clearfil S3 Bond contains water to alleviate the need for a surface with a specific degree of wetness and to resist hydrolysis, providing for a lasting and reliable adhesion. It resists hydrolysis which provides for reliable and durable adhesion. As with other seventh-generation adhesives, G-Bond offers versatility in the degree of wetness on the tooth surface at the time of adhesive application.

**The all-in-one seventh generation adhesives are user-friendly and most offer both a bottle and a unit-dose version**

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**All-In-One Bond Dental Adhesive System**

OptiBond All-In-One is a single-component, self-etch adhesive that eliminates multiple steps when bonding direct and indirect restorations. Clinicians have everything they need for etching, priming and bonding in one material. OptiBond All-In-One is a light-cured adhesive that provides adhesion to all surfaces and substrates. Its ternary solvent system provides enhanced shelf-life stability and effective enamel etching for long-term bond performance.

According to some independent studies provided by Kerr Corporation, OptiBond All-In-One delivers excellent...
penetration into dentin tubules, offering exceptional bond strength and protection against microleakage and post-operative sensitivity.

Its unique etching capability enables the most effective enamel etching of any single-component adhesive, creating a deeper-etched surface for higher mechanical retention and chemical bonding. Scanning electron microscopy (SEM) of etched enamel shows the deep etching obtained using this capability (Figure 2), and SEM of the adhesive-dentin-bonding interface shows the deep tags that result from use of this system in dentin (Figure 3).

I have found that the low film thickness makes it easier to seat indirect restorations, creating a better fit. OptiBond All-In-One is available in both a 5 ml bottle delivery and a convenient free-standing Unidose™ device.

Case Presentations
Seventh Generation Bonding Agents are ideal for bonding indirect restorations, and for direct composite resin (where bonding is mandatory regardless of the material and technique being used).

Case Presentation 1 — Indirect Restorations
A patient sitting for an initial consultation was dissatisfied with her smile (Figure 4). Clinical examination revealed a Maryland bridge from teeth #6–#8 with failing margins (Figures 5, 6). The patient stated that the bridge had been recemented a couple of times since its original placement five years prior. Tooth #10 had an existing veneer restoration to correct a peg lateral. Also, tooth #11 and tooth #12 were inverted. Probing depths were within normal levels in the anterior region, and the patient’s periodontal health was within acceptable limits.

The Smile Guide Book (Discus Dental) was used to complete the smile analysis necessary for predesigning the case. Her existing bridge was asymmetric, and the patient preferred a more complete and uniform smile. In order to achieve this, the shape selected would be rounder and the embrasures between the teeth would be smaller. The lip line edge versus the incisal edge of the teeth suggested that the patient could tolerate lengthening of the incisal edges. The results of the smile analysis, diagnostic study models, and preoperative clinical photography were reviewed with the patient to determine the desired treatment plan for improving her smile and function. Since the patient’s complaint was extreme dissatisfaction with the whole appearance of her smile, it was decided to incorporate a metal-free bridge.
material (Lava™, 3M) for the missing lateral and porcelain veneers on the adjacent teeth. The proposed treatment plan of a zirconium bridge (Lava, 3M) from #6–#8 and porcelain veneers from #9–#11 was reviewed with the patient, and she was excited to start the treatment.

After anesthetic was administered, a diamond bur was used to prepare the anterior teeth. It was very important to adhere to the preparation guidelines for the zirconium bridge in order to ensure functional and esthetic predictability. The laboratory required a minimum of 0.8 mm reduction of the facial walls and a minimum of 1.5 mm of incisal reduction. Internal line angles were to be rounded, and a butt joint margin was required (Figure 7). Also, an ovate area was created in the gingiva at the pontic site of tooth #7 with an Odyssey® Laser (Ivoclar Vivadent) to create a more harmonious emergence profile for the pontic. Impressions were taken using a quick-setting polyvinylsiloxane (PVS) impression material (Take 1®, Kerr). These impressions, a bite registration, and photos were then forwarded to the lab for fabrication of the final restorations.

**Provisionalization**

A provisional restoration, which was significant to the overall treatment, was made from an impression of a composite mock-up. Using Fill-In™ (Kerr) temporary material, this mold was quickly filled and placed on the patient’s prepared dentition. Within a couple of minutes, the temporary had cured and was ready for shaping. Gross shaping and contouring were achieved using flexible discs (OptiDisc™, Kerr). A flame-shaped fine diamond was used to shape and trim the margins and embrasure spaces. The next day, the patient returned for evaluation of size, shape, color, and bite. Already, she exhibited excitement and confidence with her provisional restorations.

**Laboratory**

During the laboratory phase, the full arch polyvinylsiloxane impressions were used to pour up a master model on which the restorations would be based. The master model was segmented into individual dies that were trimmed and pinned to determine the manner by which the final restorations would integrate with the existing soft tissue. A silicone incisal matrix of the provisional restorations was created to guide the placement of incisal effects and edge position in the subsequent ceramic buildup. In addition, comprehensive color mapping ensured that the definitive esthetic results would meet patient expectations.

**Cementation**

The patient was anesthetized and a nonlatex split-rubber dam was placed. Prior to try-in of the definitive restorations to verify fit and shade, the provisional restorations were removed and any remaining cement was cleaned off the prepared dentition using Preppies Paste. The restorations were tried in to verify marginal fit, contour, contacts, and shade (Figure 8). Following patient approval of the final restorations, the cementation process was initiated.

The veneer restorations were treated with 37 percent phosphoric acid for 20 seconds, rinsed, silanated, and air dried for one minute. OptiBond All-in-One was applied to the preparations with a scrubbing motion for 20 seconds. A second application was placed on the preparations with a scrubbing motion for 20 seconds and then gently air dried for five seconds with a medium force of air. The adhesive was light cured for 10 seconds per tooth. Since the film thickness of OptiBond All-In-One
adhesive is approximately 5 microns after curing, there was no concern during the seating process.

NX3 Nexus® Third Generation (Kerr) light-cure resin cement was applied to the veneer restorations (Figure 9).

The restorations were then placed on the preparations and, while they were firmly held in place, a rubber tip applicator removed all excess luting cement from the margins. A thin layer of glycerin was then applied to the margins to prevent the formation of an oxygen-inhibiting layer. The restorations were tacked at the gingival margin. Once the veneer restorations were placed, the bridge restoration was seated using Maxcem (Kerr) resin cement.

While the restorations were still firmly held in place, the restored dentition was flossed and any excess luting cement was carefully removed. Once the majority of the excess cement was removed, the restored dentition was completely light-cured from both the facial and lingual sides. Any residual cement was removed with a #15 scalpel and finished with a fine diamond and polishing points. The occlusion was verified and adjusted. Overall health and structure of the soft tissue and restorations were very good. As seen in the postoperative photos immediately after seating, the restorations exhibited a nice esthetic look and the patient was extremely happy (Figures 10–12). Also, upon review two weeks later, the patient had no complaints of sensitivity.

Case Presentation 2 — Direct Composite Restorations

A patient sitting for an initial consultation was concerned about some sensitivity on the left-hand side in her upper back teeth. Clinical examination revealed that the occlusal amalgam restorations on tooth #14 and tooth #15 were defective, with leaking margins. The two teeth also had fractures adjacent to the amalgams, caries was evident, and a mesial defect was present on tooth #15 (Figure 13). All other teeth were clinically sound, there was no recession present, the patient’s periodontal health was within acceptable limits, and she had no other complaints.

After discussion on the available options utilizing the DemoDent anatomical model (DemoDent PLLC), the patient elected to have the restorations replaced with bonded composite restorations. After anesthetic was administered, diamond burs were used to remove the defective amalgams and adjacent caries (Figure 14).

Upon removal of the amalgams, it was found that caries was present in the deepest regions of the preparations. This was carefully removed using a slow-speed handpiece with large round burs. The preparations were extended to remove the caries in the palatal fissure regions, and to prepare the mesial box in tooth #15. A sectional matrix band (Garrison) was placed over the mesial margin of tooth #15 in such a way that its position and shape would
enable placement of a composite with an optimal mesial contour. Once tooth #15 was isolated by the matrix band, both molars were dried and an all-in-one adhesive (OptiBond All-in-One) was applied to the preparations and adjacent enamel for 20 seconds, and then gently air dried for five seconds (Figure 15).

The restorations were completed using light-cured flowable composite (Premise flow and Premise, Kerr), after which the matrix band was removed, the occlusion was verified and adjusted, and the restorations were finished and polished (Figure 16).

Summary
Dental adhesives have dramatically changed the options available for restoration placement since their introduction more than forty years ago. Initially, these required a longer etching time and were only recommended for etching and bonding of the enamel. Dental adhesive developments shortened the etching time and enabled etching and bonding of dentin as well as enamel. However, early generation adhesives had weaker bond strength and allowed marginal leakage at the restoration margin. Today, clinicians have a variety of esthetic and functional materials to choose from when faced with the need to perform cosmetic dentistry. As dentists, we are always looking for products that are quick and simple to use yet high-performing and effective. OptiBond All-In-One single component self-etching dental adhesive and other similar seventh-generation adhesives offer great benefits, whether used as the main adhesive or as an adjunctive bonding agent. The versatility of seventh-generation dental adhesives enables their use for both indirect and direct restorations, providing for excellent marginal seal and high bond strength.

References

Author Profile
Ara Nazarian, DDS, is a graduate of the University of Detroit-Mercy School of Dentistry. Upon graduation he completed an AEGD residency in San Diego, Calif., with the United States Navy. He is a recipient of the Excellence in Dentistry Scholarship and Award. Currently, he maintains a private practice in Troy, Mich., with an emphasis on comprehensive and restorative care. His articles have been published in many popular dental publications. Dr. Nazarian also serves as a clinical consultant for the Dental Advisor., testing and reviewing new products on the market. He has conducted lectures and hands-on workshops on esthetic materials and techniques throughout the Untied States. Dr. Nazarian is also the creator of the DemoDent patient education model system. He can be reached at 248.457.0500 or at www.demo-dent.com.

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Questions

1. The technique of etching enamel with phosphoric acid was first introduced to dentistry by _________.
   a. G.V. Black
   b. Lindhe
   c. Buonocore
   d. none of the above

2. In 1999, approximately ________ direct resin restorations were placed.
   a. 25 million
   b. 46 million
   c. 75 million
   d. 86 million

3. The first- and second-generation bonding agents used during the 1960s and 1970s _________.
   a. did not recommend etching the dentin
   b. allowed dentin leakage with clinical margin stain
   c. relied on adhesion to the attached smear layer
   d. all of the above

4. Third-generation adhesive systems were introduced _________.
   a. in the 1960s
   b. in the 1970s
   c. in the 1980s
   d. none of the above

5. Third-generation adhesive systems _________.
   a. introduced acid etching of dentin
   b. decreased dentin margin failure
   c. increased bond strength over first- and second-generation systems
   d. all of the above

6. Fourth-generation adhesive systems formed a “hybrid” layer of collagen and resin.
   a. True
   b. False

7. ________ and ________ described the penetration of resin into dentin as giving high bond strengths and a dentin seal.
   a. Fusayama; Buonocore
   b. Nakabayashi; Haggag
   c. Fusayama; Nakabayashi
   d. none of the above

8. The idea of “wet bonding” was introduced by _________.
   a. Tanika
   b. Kanca
   c. Fusayama
   d. all of the above

9. An advantage of fourth-generation adhesive systems over earlier adhesive systems was that they significantly reduced margin leakage.
   a. True
   b. False

10. A disadvantage of fourth-generation adhesive systems was _________.
    a. the complexity of multiple bottles and steps
    b. the higher bond strength achieved
    c. the very technique-sensitive nature of the system
    d. a and c

11. Fifth-generation bonding systems _________.
    a. were introduced during the mid 1990s
    b. combined primer and adhesive in one bottle
    c. were used only to etch enamel
    d. a and b

12. Unit-dose packaging was introduced _________.
    a. with third-generation adhesive systems
    b. with fourth-generation adhesive systems
    c. with fifth-generation adhesive systems
    d. all of the above

13. The bond strength to dentin and enamel of sixth-generation adhesive systems _________.
    a. was higher than in fourth- and fifth-generation adhesive systems
    b. was lower than in fourth- and fifth-generation adhesive systems
    c. was equal to that in fourth- and fifth-generation adhesive systems
    d. a and b

14. Attributes of an ideal bonding agent include _________.
    a. high bond strength
    b. thin film thickness, to ensure easy and complete seating of restorations
    c. post-placement stability
    d. all of the above

15. The leading reason for replacement of existing restorations is _________.
    a. restoration fracture
    b. secondary caries
    c. discoloration of the restoration
    d. all of the above

16. “All in one” adhesives combine ________ in a single solution.
    a. etch, bond, and restoration
    b. etch, prime, and bond
    c. water, etch, and prime
    d. none of the above

17. Seventh-generation bonding systems were introduced in _________.
    a. 1999
    b. 2001
    c. 2002
    d. 2004

18. ________ is a key attribute in dental adhesives.
    a. High pH
    b. Shear bond strength
    c. Marginal detection
    d. all of the above

19. A ternary solvent system provides enhanced shelf-life stability and effective enamel etching for long-term bond performance.
    a. True
    b. False

20. Penetration of an adhesive system into dentin tubules _________.
    a. offers protection against microleakage
    b. offers protection against postoperative sensitivity
    c. offers exceptional bond strength
    d. all of the above

21. Deep penetration of an adhesive into dentinal tubules is evidenced on SEM by _________.
    a. areas of remineralization
    b. deep resin tags
    c. wider tubules
    d. none of the above

22. Low adhesive film thickness makes it easier to seat indirect restorations.
    a. True
    b. False

23. Adhering to the preparation guidelines for zirconium bridges is very important _________.
    a. to ensure aesthetic predictability
    b. to ensure that soft tissue does not need to be retracted
    c. to ensure functional predictability
    d. a and c

24. An ovate area can be created in the gingiva at the site of a pontic to _________.
    a. create a more harmonious emergence profile for the pontic
    b. reduce the amount of porcelain palatally
    c. help reduce caries
    d. none of the above

25. In the laboratory, a silicone incisal matrix of provisional restorations can be used to _________.
    a. guide the placement of incisal effects
    b. guide the placement of edge position in the subsequent ceramic buildup
    c. cut a corner
    d. a and b

26. According to the article, veneer restorations can be etched _________.
    a. with 37 percent phosphoric acid for 20 seconds
    b. with 57 percent phosphoric acid for 60 seconds
    c. with lactic acid for 45 seconds
    d. none of the above

27. All direct resin restorations are candidates for dentin bonding.
    a. True
    b. False

28. All seventh-generation adhesive systems are available in both bottle and unit-dose versions.
    a. True
    b. False

29. Fluoride-releasing bonding agents are designed to _________.
    a. promote demineralization
    b. help prevent secondary caries
    c. increase salivary flow
    d. all of the above

30. The versatility of seventh-generation dental adhesives _________.
    a. enables their use in both indirect and direct restorations
    b. provides excellent marginal seal
    c. provides high bond strength
    d. all of the above
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THE PROGRESSION OF DENTAL ADHESIVES

Educational Objectives

1. Be knowledgeable about the evolution of bonding adhesives
2. Know the attributes of an ideal bonding agent
3. Be knowledgeable about the properties of the seventh-generation adhesives and the advantages they offer
4. Know the applications that seventh-generation adhesives can be used for and understand the techniques that should be used

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Objective #1: Yes No
Objective #2: Yes No
Objective #3: Yes No

2. To what extent were the course objectives accomplished overall?
5 4 3 2 1 0

3. Please rate your personal mastery of the course objectives.
5 4 3 2 1 0

4. How would you rate the objectives and educational methods?
5 4 3 2 1 0

5. How do you rate the author’s grasp of the topic?
5 4 3 2 1 0

6. Please rate the instructor’s effectiveness.
5 4 3 2 1 0

7. Was the overall administration of the course effective?
5 4 3 2 1 0

8. Do you feel that the references were adequate?
Yes No

9. Would you participate in a similar program on a different topic?
Yes No

10. If any of the continuing education questions were unclear or ambiguous, please list them.
_________________________________________________________________________________________________________

11. Was there any subject matter you found confusing? Please describe.
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