International Journal of Adhesion & Adhesives 49 (2014) 109–114

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Bond strength, biaxial flexural strength and flexural modulus of dentin bonding systems exposed to water

A.O. Carvalho [a], M.R.O. Carrilho [b], F.A. Rueggeberg [c], G.M.B. Ambrosano [d], M. Giannini [a,*]

[a] Department of Restorative Dentistry, Piracicaba Dental School, Campinas State University, Piracicaba, SP, Brazil
[b] Biomaterials Research Group, Bandeirante University of São Paulo, GEO/UNIBAN, São Paulo, SP, Brazil
[c] Department of Oral Rehabilitation, School of Dentistry, Georgia Regents University, Augusta, GA, USA
[d] Department of Social Dentistry, Piracicaba Dental School, Campinas State University, Piracicaba, SP, Brazil

ARTICLE INFO

Article history:
Accepted 30 October 2013
Available online 19 December 2013

Keywords:
Bonding agents
Bond strength
Biaxial flexural strength
Modulus

ABSTRACT

Purpose: This study evaluated the effects of storage time on dentin bond strength, biaxial flexural strength, and flexural modulus of four adhesive systems.
Materials and Methods: The following adhesive systems were tested: Easy Bond, Scotchbond SE, Single Bond Plus, and Scotchbond Multi-Purpose. Sixty human third molars were used for the microtensile bond strength test ($n=15$). The adhesives were applied to flat occlusal dentin surfaces according to the manufacturers' instructions and a Filtek Supreme resin composite block (6 mm high) was incrementally built up. After 24 h, the teeth were prepared for the bond strength test. The specimens were stored for one week, six months, and one year in distilled water. At the end of each storage period, the specimens were tested under tension (0.5 mm/min) until failure occurred. For the biaxial flexural test, resin discs of each adhesive (0.6 mm thick and 6.0 mm in diameter) were prepared in silicon molds ($n=10$). The discs were stored for the same storage periods in distilled water prior to testing in a universal testing machine (1.27 mm/min). Data were analyzed using two-way analysis of variance and Tukey's test ($\alpha=0.05$).
Results: Bond strength values decreased significantly after six months and one year of water storage only for Scotchbond SE (from 48.1 ± 11.0 to 24.5 ± 15.3 MPa after one year). The storage time did not affect the flexural strength or modulus for any adhesive tested.
Conclusion: Water storage for six months or one year can reduce the dentin bond strength of adhesives; however, the results are product-dependent. No changes in flexural strength or modulus of the adhesives tested were observed after storage of any duration.

1. Introduction

The current classification of dentin bonding agents is based on the adhesion strategy and number of clinical application steps. Depending on the bonding strategy, the adhesives can be etch-and-rinse or self-etching systems, and according to clinical application, they are classified as one, two, or three steps. The first step for the application of an etch-and-rinse adhesive involves phosphoric acid etching, rinsing, and moisture control of the conditioned dentin surface. Subsequently, when using a three-step etch-and-rinse adhesive, a priming step is required, followed by the application of a hydrophobic adhesive resin [1].

Simplified two-step etch-and-rinse adhesives combine the primer and adhesive resin components. Given that three- and two-step etch-and-rinse adhesives are developed and produced by the same manufacturers, most of these bonding agents present similar compositions regarding solvents and adhesive monomers. Nevertheless, despite their similar compositions, *in vitro* and *in vivo* bonding effectiveness data from these etch-and-rinse adhesives have shown that ethanol/water-based, three-step etch-and-rinse adhesives are considered the "gold standard" materials in terms of bonding durability [2–6].

Whereas micro-mechanical interlocking associated with hybrid layer formation is the main bonding mechanism for etch-and-rinse adhesive systems, some self-etching adhesives contain acidic monomers, such as 10-MDP, 4-META and MAC-10, which are able to chemically bond to mineralized dental tissues [7–10]. These acidic monomers form an ionic bond with the calcium in hydroxyapatite crystals, providing additional adhesion for some self-etching adhesives [3,11,12]. Simplified adhesives that combine self-etching primers with the hydrophobic adhesive resin in only one application are known as "all-in-one" or one-step self-etching adhesives. Although there is a tendency towards the simplification of adhesive solutions and bonding

* Correspondence to: Department of Restorative Dentistry, Piracicaba Dental School, State University of Campinas, Av. Limeira, 901 Areião, Piracicaba, SP, 13414-903, Brazil. Tel.: +55 1 921 065 340; fax: +55 1 921 065 218.
E-mail address: giannini@fop.unicamp.br (M. Giannini).

0143-7496/$ - see front matter © 2014 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.ijadhadh.2013.12.017

procedures, inadequate performance of early one-step self-etching adhesives reported as a result of some scientific studies has limited the clinical use of this type of adhesives [3,6,11,13].

Adhesives are important to bond resin-based restorative materials to enamel and dentin. Thus, they must possess a high bond strength to tooth structure, a degree of conversion and adequate mechanical properties such as elastic modulus and strength to resist occlusal loading and hydrolytic degradation. Measurements of such mechanical properties as well as dentin bond strength can provide important information about the different types or categories of adhesive systems. The aim of this study was to analyze four adhesive systems, representing different bonding strategies, to assess their mechanical properties and long-term bonding effectiveness when exposed to water. The null hypotheses to be tested were (1) that adhesives with different application modes would not show significant differences in dentin bond strength, biaxial flexural strength, or flexural modulus and (2) that long-term water storage would not affect the bond strength, biaxial flexural strength, or modulus of any adhesive.

2. Materials and methods

2.1. Microtensile bond strength

Sixty caries-free recently extracted human third molars stored in 0.1% thymol solution at 4 °C were used for analysis. The teeth were obtained under a protocol approved by the review board of the Piracicaba Dental School (#146/2010). Occlusal enamel and roots were removed using a diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water lubrication to expose a middle-depth dentin surface parallel to the occlusal surface. Flat dentinal surfaces were wet abraded with 600-grit silicon carbide paper (3M of Brazil, Sumaré, SP, Brazil) for 10 s to create a standardized smear layer. The surfaces were randomly divided into four groups according to the different adhesive systems ($n=15$).

Four commercially available dentin adhesive systems (Table 1) were tested: a one-step self-etching (Easy Bond), two-step self-etching (Scotchbond SE), two-step etch-and-rinse (Single Bond Plus), and three-step etch-and-rinse (Scotchbond Multi-Purpose) adhesive (3M ESPE, St. Paul, MN, USA).

The adhesive systems were applied according to the manufacturers′ instructions. Following application, a resin composite block (6 mm high) was incrementally built up in three layers with Filtek Supreme (3M ESPE, St. Paul, MN, USA, lot number: N118032) onto the bonded dentin surfaces. Each incremental layer was light cured for 20 s (irradiance of 620 mW/cm^2, XL 3000, 3M ESPE, St. Paul, MN, USA), monitored by radiometer (Demetron Optilux Radiometer, Kerr Corp. Orange, CA, USA). The teeth were then stored in distilled water at 37 °C for 24 h.

The bonded teeth were prepared for microtensile testing using the "non-trimming" technique [14]. Each tooth was vertically and serially sectioned into 0.9-mm thick slices using the same diamond saw under water lubrication. Each slice was then further sectioned to produce twelve bonded specimens of approximately 0.9 mm^2. Four bonded samples were stored in distilled water for one week, four for six months, and another four specimens for one year. In the groups that were stored in water for six months and one year, the water was changed monthly.

At the end of each storage period, the bonded specimens were fixed to the grips of a microtensile testing device using cyanoacrylate glue (Super Bonder Gel, Henkel/Loctite, Diadema, SP, Brazil) and tested under tension at a cross-head speed of 0.5 mm/min until failure in a universal testing machine (Ez-Test, Shimadzu, Kyoto, Japan). After fracture, the specimen was removed from the testing apparatus and the cross-sectional area at the site of fracture was measured with a digital caliper (Starrett Ind. Com. Ltda., Itu, SP, Brazil) to calculate the tensile bond strength. A single failure stress value was then calculated for each tooth by averaging the values of the four bonded slices from that tooth (a total of 720 specimens tested). Bond strength data were analyzed by split-plot two-way analysis of variance (ANOVA) followed by Tukey′s test (with a preset alpha of 0.05), considering adhesive and storage time as variables.

Fractured surfaces of the tested specimens were allowed to air-dry overnight at 37 °C, after which they were sputter-coated with gold (MED 010, Balzers, Balzer, Liechtenstein) and examined by a single individual using a scanning electron microscope (VP 435, Leo, Cambridge, UK). Failure patterns were classified as (1) cohesive within the composite, (2) cohesive within the adhesive layer, (3) cohesive within the dentin, (4) adhesive along the dentin surface, (5) mixed when simultaneously exhibiting dentin surface, adhesive layer and remnants of composite. Representative areas of the failure patterns were photographed at 90 × magnification.

2.2. Biaxial flexural strength and flexural modulus

Adhesive solutions from each adhesive bottle were dispensed into a mixing well and air-dried for 20 s to allow the organic

Table 1
Composition of adhesive systems used.

Adhesive (classification)	**Composition** (% by weight)	**Lot number**
Adper Easy Bond (one-step self-etching)	Bisphenol A diglycidyl ether dimethacrylate (15–25%), 2-hydroxyethyl methacrylate (15–25%), ethanol (10–15%), water (10–15%), phosphoric acid-6-methacryloxy-hexyl esters (5–15%), silane treated silica (8–12%), 1,6-hexanediol dimethacrylate (5–10%), copolymer of acrylic and itaconic acid (1–5%), (dimethylamino) ethyl methacrylate (1–5%), camphorquinone (1–3%), 2,4,6-trimethylbenzoyldiphenylphosphine oxide (1–3%)	362007
Adper Scotchbond SE (two-step self-etching)	Liquid a: water (70–80%), 2-hydroxyethyl methacrylate (10–20%) Liquid b: surface treated zirconia (15–25%), triethylene glycol dimethacrylate (15–25%), di-hema phosphates (10–15%), mono hema phosphate (5–10%), methacrylated pyrophosphates (5–10%), tri hema phosphate (< 3%), phosphoric acids-6-methacryloxy-hexyl esters (5–10%), 1,6-hexanediol dimethacrylate (< 4%), diurethane dimethacrylate (1–10%), trimethylolpropane trimethacrylate (5–15%), ethyl 4-dimethyl aminobenzoate (< 2%), dl-camphorquinone (< 2%)	a: 9BU b: 9BW
Adper Single	Etchant: water (55–65%), phosphoric acid (30–40%), synthetic amorphous silica (5–10%).	Etchant: 9NL
Bond Plus (two-step etch-and-rinse)	Adhesive: ethyl alcohol (25–35%), silane treated silica (nanofiller) (10–20%), bisphenol A diglycidyl ether dimethacrylate (10–20%), 2-hydroxyethyl methacrylate (5–15%), glycerol 1,3-dimethacrylate (5–10%), copolymer of acrylic and itaconic acids (5–10%), water (< 5%), diurethane dimethacrylate (1–5%)	Adhesive: 9WP
Adper Scotchbond Multi-Purpose (three-step etch-and-rinse)	Etchant: Water (55–65%), phosphoric acid (30–40%), synthetic amorphous silica (5–10%) Primer: Water (40–50%), 2-hydroxyethyl methacrylated (35–45%), copolymer of acrylic and itaconic acids (10–20%) Adhesive: Bisphenol A diglycidyl ether dimethacrylate (60–70%), 2-hydroxyethyl methacrylate (30–40%)	Etchant: 9NL Primer: 9CE Adhesive: 9RM