Bond Strength and Monomer Conversion of Bonding Agents Mixed with Restorative Composites Prior to Light Exposure

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This study examined the effect of adhesive systems (either placed as directed or when mixed with composites prior to photocuring) on bond strength and monomer conversion. Occlusal surfaces of extracted human molars were ground flat and Scotchbond Multipurpose®, Single Bond®, or Clearfil SE Bond® adhesive systems were applied according to manufacturer's directions, mixed in situ with flowable or hybrid composites prior to photocuring. Specimens were prepared for microtensile bond-strength testing, and maximal bond strength at failure was recorded. Adhesives and composites were also placed on a diamond attenuated-total-reflectance unit, and infrared spectra were obtained kinetically. Addition of flowable Scotchbond prior to light-curing increased bond strength; however, no effect on Single Bond and Clearfil SE Bond was observed. The mixture of adhesives with composites resulted in lower monomer conversion for Scotchbond and Clearfil SE Bond.

1. INTRODUCTION

Conventional dental restorative treatment with resin-based materials dictates placement of a bonding agent to etched, resin-primed, demineralized tooth tissue [1–3]. The adhesive system is typically spread into a thin layer after application and prior to light exposure to minimize pooling, evaporate solvent carrier, and provide a minimal thickness of unfilled adhesive resin. The adhesive system is then photocured, and resin composite is incrementally placed and polymerized. However, this methodology raises the potential for the resulting resin–dentin bond to be less than optimal [4–6]. Such application may result in formation of a linear or very low cross-linked and unfilled polymer matrix in the hybrid layer [7,8] and the inhibition of atmospheric oxygen on adhesive resin polymerization of such a thin, low-viscosity bonding layer.

Formation of a durable polymer network to surround exposed collagen and covalently bond to the restorative resin placed on top is not an easy task. This process starts by placement of primer agents. Often, these primers are monofunctional monomers contained in an organic solvent (ethanol or acetone). Use of an air spray accelerates solvent evaporation, usually leaving only the priming resin [2]. If high levels of water remain, polymerization will be greatly inhibited and a well-defined polymer matrix will not develop [9]. Under the worst-case scenario, the more hydrophobic monomer may form small spheres within the water film left and react to polymerize as isolated beads instead of an intertwined, linear polymer matrix [10].

Monofunctional monomers are less hydrophobic than are multifunctional ones. Thus, because most of the initial priming monomers are monofunctional, the polymer matrix formed has lower physical properties than it would have if more hydrophobic and multifunctional monomers were present and capable of providing cross-linking [11]. If the bonding agent is placed, air sprayed into a thin layer, and then mixed *in situ* with a small amount of restorative resin (flowable or conventional composite), potential benefits may arise. It may be possible to obtain a more highly cross-linked and filled polymer network surrounding exposed collagen, which may increase resin properties. Such increase may result in enhanced bond strength, lower permeability, and greater durability of the resin–dentin bond than when using conventional methods of placing and exposing each material separately.

Thus, the dentin bonding system would be used more as a wetting agent to enhance application of subsequently placed, more hydrophobic composite. The anticipated increase in cross-linking within the hybrid layer may impart higher strength and durability to the resin–dentin bond than when using conventional placement and curing methods. However, such a combination may behave differently depending on adhesive system type, because of the differences in chemistries and application techniques.

This research examined the effect of placing commercially available dentin bonding systems in a conventional manner as opposed to placement of the bonding agents and mixing *in situ* with a small amount of composite prior to the initial light exposure. Microtensile bond strength, monomer conversion, and changes in the infrared absorption ratio of aliphatic to aromatic C=C peaks of uncured resin systems materials were determined when placed as directed or when premixed with resin composite (flowable or hybrid). The research hypotheses tested were that exposure of bonding agent and composite mixed together would result in (1) enhanced tensile bond strength of restorative materials to human dentin and (2) greater monomer conversion.

2. EXPERIMENTAL

2.1. Materials Used

The adhesive systems used are presented in Table 1. These agents were selected to represent a three-step etch-and-rinse conventional adhesive system (Scotchbond Multipurpose®), an etch-and-rinse single-bottle adhesive (Single Bond®), and a nonrinse self-etching primer (Clearfil SE Bond®). Bonding agents were applied using manufacturers' recommended methods, and were light cured ($600\,mW/cm^2$) for $10\,s$ using a conventional quartz–tungsten–halogen light source (XL 3000®, 3M ESPE, St. Paul, MN, USA). Specimens were also made when mixing the placed, uncured dentin bonding agents ($0.005\,mL$) with $0.025\,mg$ of restorative composite (flowable or hybrid) for $10\,s$ prior to initial light curing. For Scotchbond Multipurpose and Clearfil SE Bond, the primer and the bond resin were applied separately, and the resin composite was applied and agitated on the dentin surface (bond strength test) and diamond surface (monomer conversion). Then, the mixture was light cured for $20\,s$ and treated as if it was only the dentin bonding agent itself. The restorative composites used consisted of a flowable composite (Filtek Flow®, 3M ESPE; composition: bisphenol A diglycidyl ether dimethacrylate, triethylene glycol dimethacrylate, bisphenol A polyethylene glycol diethers

TABLE 1 Composition and Application Steps of Adhesive Systems

Adhesive system	Composition[a] (lot number)	Application steps[b] (monomer conversion/ bond test)
Scotchbond Multi-Purpose® (3M ESPE, St. Paul, MN, USA)	Primer: HEMA, PAA, and water (5KP). Adhesive: Bis-GMA, HEMA, and CQ (7HJ).	d, e, f, g/a, b, c, d, e, f, g
Single Bond® (3M ESPE, St. Paul, MN, USA)	Adhesive: Bis-GMA, HEMA, PAA, dimethacrylates, CQ, ethanol, and water (3JC).	e, c, g/a, b, c, e, c, g
Clearfil SE Bond® (Kuraray Medical Inc., Kurashiki, Okayama, Japan)	Primer: MDP, HEMA, hydrophilic dimethacrylate, N,N-Diethanol p-toluidine, and water (00447A). Bond: MDP, Bis-GMA, HEMA, hydrophobic dimethacrylate, CQ, N,N-diethanol p-toluidine, and silanated colloidal silica (00593B).	d, c, e, f, g/d, c, e, f, g

[a]Abbreviations: MDP, 10-methacryloyloxy methacrylate; CQ, camphorquinone; HEMA, 2-hydroxyethyl methacrylate; Bis-GMA, bisphenol-glycidyl methacrylate; PAA, polyalkenoic acid copolymer.
[b]Application steps: a, acid etching; b, wash with water; c, gently air dry; d, apply primer; e, apply adhesive; f, well mixed (primer and adhesive); g, light-cure. According to manufacturer's instructions.

dimethacrylate, and silica-zirconium oxide) or a conventional restorative, hybrid resin composite (Filtek Z250®, 3M ESPE, composition: bisphenol A polyethylene glycol diether dimethacrylate, diurethane dimethacrylate, bisphenol A diglycidyl ether dimethacrylate, triethylene glycol dimethacrylate, and silica–zirconium oxide).

2.2. Microtensile Bond Strength

Extracted, caries-free human third molars were used in this study, according to protocols approved by the institutional review board of the Piracicaba School of Dentistry, University of Campinas (37/2003). Eighteen third molars were transversally sectioned with a diamond disc (Isomet®, Buehler Ltd., Lake Bluff, IL, USA) under water lubrication to expose flat, midcoronal dentin surfaces. Tooth roots were severed, and the crown sections were longitudinally cut (mesio-distally and buccal-lingually) into four quarters. Seventy-two tooth specimens were thus generated and were then randomly assigned to one of nine experimental groups tested ($n = 8$).

Immediately before bonding, a smear layer was created on the exposed dentin surface by wet polishing with 600-grit SiC paper for 30 s. Each of the three bonding systems previously described was applied to dentin using manufacturer's recommended directions and was then light cured for 10 s. The modified procedures for premixing composite were used as previously described.

Resin composite buildups were constructed incrementally on the polymerized bonding agent in five 1-mm-thick layers using a hybrid composite (Z250, 3M ESPE). Each layer was light cured for 40 s using the same light-curing unit as before. Restored teeth were stored in distilled water at 37°C for 24 h. Tooth fragments with bonded composite were obtained by vertically sectioning the tooth serially in both x and y directions across the bonded interface to obtain several bonded beams measuring 0.8 mm^2 in cross-section. Three beams were randomly selected from each bonded tooth fragment to compose each testing group. Each bonded beam was fixed to the grips of a microtensile testing device with cyanoacrylate glue (Zapit®, DVA, Corona, CA, USA) and tested in tension at 0.5 mm/min until failure in a universal testing machine (4411, Instron Co., Canton, MA, USA). After fracture, the cross-sectional area of the debonded interface was measured to the nearest 0.01 mm with a digital caliper (Starret 727-6/150®, Starret, Itu, SP, Brazil) and used to calculate test results in units of stress (MPa). Means of the three beams were calculated for each restored tooth fragment. Data were analyzed statistically by two-way Analysis of Variance (ANOVA) and the Tukey–Kramer post hoc test. Statistical significance was established at $\alpha = 0.05$.

2.3. Monomer Conversion

The test method measured monomer conversion at a simulated interface of dentin and bonding resin. For that purpose, a horizontal diamond attenuated-total-reflectance unit (ATR) was used (MKII Golden Gate, SPECAC LTD, Kent, Great Britain). A 5-mm-diameter hole was punched in a piece of 0.25-mm-thick adhesive tape. The tape was positioned so that the ATR element was in the center of the hole. The adhesive systems were applied into this hole following manufacturer's directions and simulating the typical clinical scenario of applying bonding agents. A piece of Mylar® was placed on the adhesive layer, and the bonding agents were light cured for 10 s using a conventional quartz–tungsten–halogen light source (3 M ESPE, St. Paul, MN, USA) that was positioned 3 mm from the diamond surface.

When testing the effect of addition of flowable (Filtek Flow, 3M ESPE) or hybrid (Shade A2, Filtek Z250, 3M ESPE) composite to the applied bonding material, a small amount of either product was placed

within the hole and mixed thoroughly with the previously placed, uncured bonding agent using a plastic applicator instrument. A piece of Mylar was then placed on top, and a glass slide was used to apply pressure and force excess material to extrude providing consistent resin thickness equivalent to that of the tape matrix. The mixture was light cured for 20 s at the same curing tip distance.

Infrared spectra were collected in the kinetic mode at a rate of one-per-second using a Fourier transform infrared (FTIR) spectrometer (FTS-40, Digilab/BioRad, Cambridge, MA, USA) at $2\,cm^{-1}$ resolution between 1680 and $1550\,cm^{-1}$. The first four collected scans served to supply the infrared spectra of the uncured resin. On the fifth second of recording, the composite was light-activated for the prescribed time while spectra continued to be collected. Data recording continued after the light was cycled off for 30 s from light initiation. Five replications for each test condition were made.

Standard methods of determining monomer conversion were used. These methods utilize changes in the ratios of aliphatic-to-aromatic C=C absorption peaks in the uncured and cured states. By comparing changes in the ratios of these two peak heights in the cured and uncured monomer states, the degree of monomer conversion into polymer was calculated [12–14]. The aliphatic C=C/aromatic C=C ratios of resins in the uncured states when bonding resin was placed by itself, or when mixed with restorative composite, were also evaluated. Only intrabrand conversion values were determined, and conversion values were compared using one-way ANOVA. Mean conversion values of each test group were correlated with the respective bond strength values and analyzed by linear regression. Statistical significance was established at $\alpha = 0.05$.

3. RESULTS

Mean tensile bond strength and monomer conversion values are presented in Tables 2 and 3, respectively. All adhesive systems applied

TABLE 2 Mean (sd) Microtensile Bond Strengths (MPa) of Adhesive Systems to Dentin

Treatment	Scotchbond®	Single Bond®	SE Bond®
As directed	26.0 (6.8) A a	28.7 (7.7) A a	32.8 (9.3) A a
With flowable	41.2 (8.9) B a	34.4 (11.3) A b	29.3 (9.1) A b
With composite	27.8 (7.6) A a	27.2 (9.6) A a	16.1 (5.8) B b

Note: Values having similar letters (uppercase, within adhesive system; lowercase, within treatment) were not statistically different.

TABLE 3 Effect of Application Method on Monomer Conversion and Uncured Infrared Absorption Ratio, Mean (SD)

Adhesive	Use	Cure @ 40 s (%)	Uncured peak absorbance ratio of aliphatic-to-aromatic C=C
Scotchbond®	As directed	60.5 (0.3) a	1.49 (0.03) a
	With flowable	58.1 (2.3) ab	1.86 (0.05) b
	With composite	56.4 (2.4) b	1.53 (0.08) a
Single Bond®	As directed	56.0 (1.7) a	2.40 (0.04) a
	With flowable	51.4 (1.5) a	2.27 (0.05) a
	With composite	51.4 (4.9) a	1.76 (0.11) b
Clearfil SE Bond®	As directed	72.5 (0.4) a	1.61 (0.02) a
	With flowable	49.9 (1.4) b	1.44 (0.02) b
	With composite	50.8 (2.3) b	1.46 (0.03) b

Note: Within an adhesive system, conversion or uncured ratio values having similar lowercase letters were not statistically different.

as directed showed similar tensile bond strengths ($p > 0.05$). Scotchbond mixed with flowable composite prior to light activation increased bond strength and exhibited higher strength than Single Bond and Clearfil SE Bond ($p < 0.05$). When SE Bond was mixed with the hybrid composite, the bond strength decreased ($p < 0.05$) and was the lowest among all groups ($p < 0.05$). The tensile bond strength for Single Bond was not affected by mixture with flowable or with restorative composite ($p > 0.05$).

For all materials tested, monomer conversion values remained the same or decreased with addition of either flowable or hybrid composite. The uncured ratio varied among test groups. Correlating bond strength and conversion values of similar treatments did not indicate a significant relationship between these two parameters ($r^2 = 0.0998$).

4. DISCUSSION

The first research hypothesis was partially upheld: that only the addition of flowable composite to Scotchbond bonding system would increase bond strength to dentin. No significant differences in bond-strength values were observed when agents were used as directed. However, when adhesive systems were mixed with composites, different behaviors were seen: bond strength and monomer conversion for Single Bond were not affected, while for Clearfil SE Bond both values were reduced after mixing. For Scotchbond, addition of the hybrid

composite did not affect bond strength but reduced monomer conversion.

The type of adhesive system used seemed to influence test results: Scotchbond is a three-step conventional system and has more hydrophobic components in the adhesive bottle than does Single Bond, which is a two-step, one-bottle primer–adhesive system. For Scotchbond, the mixture of two hydrophobic materials (the bonding resin of Scotchbond adhesive + flowable composite) formed an adequate hybridization process and produced high bond strength. On the other hand, Clearfil SE Bond is a self-etching, two-step product, containing a self-etching primer and an adhesive bottle containing filler particles. Studies have shown an adverse interaction between the tertiary amine catalytic component of restorative composites placed over an uncured acidic adhesive resin layer that can compromise resin–dentin bonding [4–6]. Clinically, these interactions could occur if low pH adhesive systems (such as Clearfil SE Bond) are used before application of a chemical-cured composite resin or if activation of light-cured composites is delayed. The latter event may have occurred when the more viscous hybrid composite was mixed with the uncured SE Bond adhesive layer [5,6]. Moreover, unsatisfactory results for combinations between the self-etching system and the composites can be related to the differences in compositions and chemistries due to different manufacturers.

The mixture of adhesive system with composites could have allowed some multifunctional monomers from the composites to diffuse into the hybrid layer, leading to a higher molecular weight and cross-linked polymer around exposed collagen fibrils. It is possible that the mixture with flowable composite would be better because the flowable material is less viscous than the hybrid one. Such a compositional change may have resulted in a polymer network having lower permeability and, thus a longer bond longevity [12]. Depending on the bonding agent characteristics, mixing a small amount of flowable composite after placement of the adhesive resin can be considered one application step that increased the presence of hydrophobic and cross-linkable monomers in the hybrid/adhesive layer.

The bond strength results of this present study were not as expected. Some publications have indicated that the hydrophobic photoinitiator camphoroquinone used in the majority of commercial dentin adhesives presents difficulties in penetrating the wet demineralized dentin matrix when a wet bonding protocol is used. Under these conditions, the hydrophilic monomers, *e.g.*, hydroxyethyl methacrylate (HEMA), penetrate the wet demineralized dentin matrix but without the benefit of a hydrophilic photoinitiator [15,16]. Moreover, the BisGMA hydrophobic monomer also has difficulty in penetrating,

infiltrating only a fraction of the total wet demineralized dentin matrix [15–17]. However, the analysis performed using FTIR exhibited the mixture between the adhesive and composite resins, which can be verified by the range in the uncured ratio data.

The mixtures of bonding agents with composites can alter the thickness and rigidity of adhesive layer, which are important variables in defining the restored tooth's mechanical behavior. To limit the intensity of the composite stress transmitted to the remaining tooth structure, an adhesive layer with substantial thickness is used as a lining, able to partially absorb the composite deformation [18]. A thin layer composed of a more flexible adhesive (lower elastic modulus) is as rigid as a thick layer composed of a less flexible adhesive (higher elastic modulus) [19]. The mechanical behavior of restorations using mixtures of bonding agents with composites needs to be further investigated.

The second hypothesis was rejected: mixtures of bonding agents with composites (flowable and hybrid) did not increase monomer conversion. Although one would expect higher monomer conversion values with the addition of resins containing more hydrophobic, multifunctional monomers to the bonding agents, mixtures for all materials used resulted in similar or decreased monomer conversion than when bonding agents were used as directed. Because the comonomer composition is changed when restorative composites are mixed with bonding agents, even a lower conversion value may actually result in a more cross-linked material. This behavior can be better understood by further analyzing the uncured ratios of both bonding agents and mixtures. The uncured ratio value is defined as the ratio of infrared absorbances at $1636 \, \text{cm}^{-1}$ (aliphatic C=C) to aromatic C=C ($1608 \, \text{cm}^{-1}$) in the uncured state. In itself, it has little meaning. However, when the ratio of the uncured bonding agent is compared with that when restorative composite is mixed with it prior to curing, one can get an idea of the proportionate change in aliphatic-to-aromatic ratios in the newly created comonomer mixture. A decrease in ratio compared with that of the bonding agent itself infers a relative increase in aromatic component. Such an increase indicates the presence of Bisphenolglcidye Methacrylate (Bis-GMA)-like in monomers that may confer additional network cross-linking.

Addition of flowable material to Scotchbond resulted in an increased ratio of the uncured material over that of the bonding system itself ($p < 0.05$), indicating a relative addition of aliphatic C=C component over that of aromatic bonds in the new comonomer mixture. Addition of the hybrid composite resulted in similar conversion value relative to that when the flowable composite was added, and the uncured ratio was similar to that applied as directed without the

composite ($p > 0.05$). This finding indicates no relative change in proportion of these two groups. Because of the high viscosity of hybrid composite, a homogeneous mixture was not achieved and probably virtually no hybrid resin reached the bottom of the adhesive layer, where the infrared spectra were collected.

For Single Bond, conversion values were not affected by application mode ($p > 0.05$), and the uncured ratio was reduced when premixing the adhesive with hybrid composite ($p < 0.05$). This result indicates that addition of the hybrid composite caused a proportionate increase in aromatic C=C content over that of the unaltered agent ($p < 0.05$). Clearfil SE Bond self-etching primer applied as directed presented a high conversion value after 30 s. When mixed with flowable or hybrid composite, conversion values and uncured ratios were reduced compared with that when using material according to manufacturer's directions. This behavior was not expected, because a decrease in uncured ratio indicates alteration of the comonomer mixtures with a prevailing trend toward addition of more aromatic C=C. Increase in the presence of this group indicates greater amounts of Bis-GMA-like monomers in the bonding resin.

In this study, curing times for the bonding agent alone was 10 s, following the manufacturer' instructions. Also, manufacturers recommend 20 s of composite light activation. Therefore, the curing time for the bonding agent plus composites was 20 s to respect the manufacturer recommendations for composite light activation and to ensure proper polymerization of the flowable or the hybrid composite resins. The additional time did not increase the adhesive degree of conversion. The formation of cross-linking structure at the initial stage of polymerization also reduces the diffusion of reactants at a later stage of the reaction, resulting in autodeceleration of the rate and limiting the final conversion [20].

Conflicting results were seen when comparing conversion values and uncured ratios with bond strength values. Addition of either flowable or hybrid composite to Clearfil SE Bond showed a decrease in uncured ratio. Consequently, an increase in bond strength would be expected, but a great reduction was seen instead, with addition of the hybrid composite. Also, the highly acidic MDP primer can interact with the tertiary amine from the composite, lowering the conversion ratio. However, although the addition of flowable composite to Scotchbond adhesive increased the uncured ratio, a higher tensile bond strength was obtained. This increase may be indicative of addition of a multifunctional monomer, such as triethylene glycol dimethacrylate (TEGDMA), that also helps to increase the possibility of cross-linking and thus provides increased bond-strength values.

5. CONCLUSIONS

Addition of flowable or hybrid composite to the Scotchbond or Single Bond bonding systems did not change conversion values but resulted in some of the highest strength values observed (significant for Scotchbond). Bond strength for all other materials and combinations produced equivalent values, with the exception of Clearfil SE Bond mixed with hybrid composite, which demonstrated the lowest value.

One cannot correlate conversion values with microtensile bond strength when comparing systems with different chemistries. However, addition of both composites to a self-etching system (Clearfil SE Bond) reduced the conversion values and the bond strength to dentin. Even though conversion did not increase as expected, the *in situ* addition of flowable composite to the etch-and-rinse dentin bonding systems (Scotchbond or Single Bond) had the potential to enhance or maintain the dentin–composite bond strength.

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