

# Permeability of Dental Adhesives – A SEM Assessment

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## ABSTRACT

**Objectives:** To morphologically evaluate the permeability of different commercial dental adhesives using scanning electron microscopy.

**Methods:** Seven adhesive systems were evaluated: one three-step system (Scotchbond Multi-Purpose - MP); one two-step self-etching primer system (Clearfil SE Bond - SE); three two-step etch-and-rinse systems (Single Bond 2 - SB; Excite - EX; One-Step - OS); and two single-step self-etching adhesives (Adper Prompt - AP; One-Up Bond F - OU). The mixture of primer and bond agents of the Clearfil SE Bond system (SE-PB) was also tested. The adhesives were poured into a brass mold (5.8 mm x 0.8 mm) and light-cured for 80 s at 650 mW/cm<sup>2</sup>. After a 24 h desiccation process, the specimens were immersed in a 50% ammoniac silver nitrate solution for tracer permeation. Afterwards, they were sectioned in ultra-fine slices, carbon-coated, and analyzed under backscattered electrons in a scanning electron microscopy.

**Results:** MP and SE showed slight and superficial tracer permeation. In EX, SB, and OS, permeation extended beyond the inner superficialities of the specimens. SE-PB did not mix well, and most of the tracer was precipitated into the primer agent. In AP and OU, “water-trees” were observed all over the specimens.

**Conclusions:** Different materials showed distinct permeability in aqueous solution. The extent of tracer permeation varied according to the composition of each material and it was more evident in the more hydrophilic and solvated ones. (Eur J Dent 2010;4:429-439)

**Key words:** Dental adhesives; Hydrophilicity; Solvents; Nanoleakage.

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## INTRODUCTION

Adhesive dentistry has increasingly sought simplification of procedures. Conventional multi-step adhesive systems have been replaced by “single-step” systems that are, apparently, simpler and faster to use. However, simplifying contemporary dental adhesives has occurred at the expense of an increasing incorporation of hydrophilic monomers (2-hydroxyethyl methacrylate - HEMA; 10-methacryloyloxydecyl-dihydrogen phosphate - MDP; Biphenyl dimethacrylates - BPDM; Methacryloyloxydecamethylene malonic acid - MAC-10), and organic solvents with variable volatility (acetone, ethanol and water).<sup>1</sup> Not unexpectedly, research has shown that these materials have drawn water from hydrated dentin through an apparently intact, polymerized adhesive layer.<sup>2,3</sup>

Long-term clinical evaluations have shown that restorations bonded with simplified adhesives exhibit an unsatisfactory performance, especially in terms of marginal discoloration<sup>4</sup> and loss of retention.<sup>5</sup> Recent studies revealed that simplified dental bonding agents behave as permeable membranes after polymerization,<sup>2</sup> allowing water to flow through the adhesive layer.<sup>6,7</sup> In fact, once unreacted components of adhesives are leached out due to the water diffusion through polymer chains,<sup>8</sup> minute water-filled voids are produced within the polymerized matrix, forming a permeable adhesive interface.

Multi-step dental adhesives are characterized by the application of a separate solvent-free, hydrophobic resin that is less permeable to water.<sup>8</sup> This procedure is thought to improve the connection between the dentin hybridized with hydrophilic monomers and the hydrophobic and viscous resin composite.<sup>9-11</sup> However, the bonding agent of multi-step adhesives needs to infiltrate, mix, and co-polymerize sufficiently well with the primed dentin in order to guarantee the mechanical and chemical stability of the bonded interface; otherwise, the primed dentin that is hybridized with hydrophilic resins would be prone to permeation by fluids originated from hydrated dentin via dentinal tubules.

Nanoleakage evaluations have been used to identify permeability zones in bonded interfaces.<sup>7,12,13</sup> This methodology relies on the storage of the resin-bonded specimen in a silver nitrate solution, which allows the silver ions to be carried

by water through structural nanoporosities, where these metallic ions may precipitate. Backscattering scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM) allows the identification of these nanoporosities by examining the silver precipitate deposited in the structural defects of the bonded interfaces. Silver nitrate, especially in its basic ammoniac form, is considered to be a tracer of hydrophilic and acidic groups. The ammonium groups of the diamine-silver ions are capable of replacing water from active hydrogen-bonding sites, while they may additionally react with acidic groups.<sup>14</sup> Thus, nanoleakage expression in adhesive layers may predict the permeability features of adhesives. However, as the bonding procedure varies as a function of many parameters (e.g., the adhesive’s composition, the efficiency of solvent evaporation, the nature and depth of dentin, the amount of water present in the substrate, among others),<sup>15-18</sup> it is difficult to verify whether the permeability of resin-dentin bonds is more closely related to the adhesive features or to the bonding technique. Hence, this study evaluates silver infiltration in dental adhesives without observing their application on dentin.

Considering that adhesive degradation increases with its permeability,<sup>14,19,20</sup> the aim is to evaluate the permeability of different commercial adhesive systems that are applied on dentin in single or multiple steps. The hypothesis tested was that there would not be a difference in the permeability to the silver nitrate solution among multi-step and simplified adhesives.

## MATERIALS AND METHODS

### Specimen preparation

The bonding resins of seven adhesive systems were used in this study. These systems comprise four approaches of bonding to dental hard tissues: one three-step etch-and-rinse system (Adper Scotchbond Multi-Purpose - MP); three two-step etch-and-rinse adhesive systems (Adper Single Bond 2 - SB; Excite - EX; One-Step - OS); one two-step self-etch primer system (Clearfil SE Bond - SE); and two single-step self-etch adhesives (Adper Prompt - AP; One-Up Bond F - OU). In addition, one primer+bond group (SE-PB), consisting of specimens obtained after mixing and polymerization of the primer and bond components of Clearfil SE Bond systems, was tested. The com-

position, batch number, and manufacturer of each adhesive system are listed in Table 1.

Three disk specimens were prepared for each adhesive system and for the primer+bond mixture. The uncured adhesives (approximately 200  $\mu$ L) were directly poured into a brass mold (5.8 mm diameter, 0.8 mm thick).<sup>8</sup> For the primer+bond specimens, a single drop of the primer was dispensed into the mold, which was left undisturbed for 20 s, and then the bonding resin was poured over the primer until the mold was completely filled. A micro-brush was applied to actively mix primer and bond agents. As primer solutions and some bonding agents have a certain amount of solvent and/or water in their composition, a solvent evaporation procedure was performed for all materials by using an oil/water-free air-syringe for 30 s. A glass cover slip was placed on the top of the resin to minimize atmospheric oxygen, and photo-activation was performed using a quartz-tungsten-halogen light source, operating at 650 mW/cm<sup>2</sup>, for 40 s (Elipar TriLight, ESPE, Germany). After removal from the mold, the bottom of each disk was further photo-cured for another 40 s. Any uncured resin remaining on the disk surface was cleaned off with absorbent paper. Next, the disks were pre-dried in a sealed desiccator containing fresh silica gel (at 37°C), over a three-day period. This time was used to enhance the specimens' polymerization and to permit better evaporation of residual solvent incorporated into the materials.<sup>8</sup>

#### Nanoleakage tracing and scanning electron microscopy evaluation

When the drying process was complete, specimens were immersed in a 50% ammoniac silver nitrate solution following the diamine silver impregnation protocol reported by Tay et al.,<sup>2</sup> except for the period of immersion in the tracer solution, which was extended for 48 hours. In a previous study,<sup>8</sup> it was found that fewer hydrophilic adhesives took approximately 48 hours to reach water sorption equilibrium. As silver ions were carried into polymerized adhesives by water, this period of immersion was used for all adhesives tested, instead of the 24-hour-period used by Tay et al.<sup>2</sup> Thus, the specimens were placed in the silver nitrate solution in total darkness for 48 hours to allow silver saturation of the specimens. Afterwards, they were rinsed in distilled water and immersed

in a photo-developing solution for 8 hours, while kept under a fluorescent light, so that the silver ions could be reduced into metallic silver particles. The silver-impregnated specimens were then embedded in epoxy resin for support. The prepared adhesive discs were cut along their diameter using a low-speed diamond saw (Isomet 1000 Precision Saw, Buehler, Lake Bluff, IL, USA), in order to expose the innermost surface. The exposed surfaces were dry-polished using a glass knife attached to an ultra-microtome (Sorvall Porter-Blum, MT2-B, Norwalk, USA). Several cuts were made to the exposed surface of the specimens until an adequate polish was obtained. The prepared surface was carbon-coated and analyzed at a variety of magnifications in an SEM (JEOL-5600 LV, Tokyo, Japan) under backscattered electrons at 90 kV. After this first evaluation, specimens were returned twice to the ultra-microtome in order to expose other regions of specimens that were then prepared following the steps outlined above to be observed under SEM. In this way, three different evaluations were performed for each specimen.

## RESULTS

Figures 1 to 8 depict the most characteristic patterns of silver permeation observed along the inner exposed surfaces of the different adhesives. Observation of adhesive surfaces revealed the presence of silver deposits in all evaluated materials. The amount of silver deposition varied. Some were sparsely spread on the surface of the specimen and others were severely interspersed through the entire thickness of the specimen.

The bonding resins of SE and MP (Figures 1 and 2, respectively) showed slight silver permeation over the interface with the embedded epoxy resin. No infiltration extending to the center of the specimens was observed.

Images produced for SE-PB showed two different and separate phases: one poorly infiltrated occupying the center of the specimen and another greatly infiltrated sector restricted to the upper and lower edges of the exposed surfaces (Figure 3).

SB presented two distinct types of silver deposition, one consisting of isolated and aggregated silver granules distributed along the interface with the epoxy resin and extending to the center of the specimens and another observed in the the

centers of the specimens, forming thin, elongated structures. In high magnifications, elongated structures look like thin fissures incompletely filled with silver (Figure 4).

EX presented just the granular pattern of silver deposition. An intense silver concentration can be observed along the margin of the specimen. A more sparse distribution extended a few micrometers into the center. No deposition could be seen in the center of the specimen (Figure 5).

OS exhibited an intense silver permeation distributed over the margin of the specimen and also protruding to its center as isolated granules. The reticular pattern of the deposition could be observed in all superficies evaluated, protruding through almost all of the specimen's thickness as images known as "water trees." A deformed, shrunken interface with embedded epoxy resin was observed for this material (Figure 6).

AP presented an intense silver deposition over the entire specimen, and it occurred predominantly in thin, elongated structures similar to the ones observed in the SB specimens. Cracks and irregular margins were also observed (Figure 7).

In OU micrographs, the granular pattern of deposition was predominant and was spread over the entire specimen. Permeation was more concentrated along the interface with the epoxy resin. The reticular pattern of silver deposition was also present but smaller in length and more rarely observed compared with OS (Figure 8).

### DISCUSSION

Since the wet bonding technique<sup>21</sup> became an imperative procedure when bonding resin composites to intrinsically wet acid-etched dentin, the development of new adhesive systems has been oriented toward making them technically

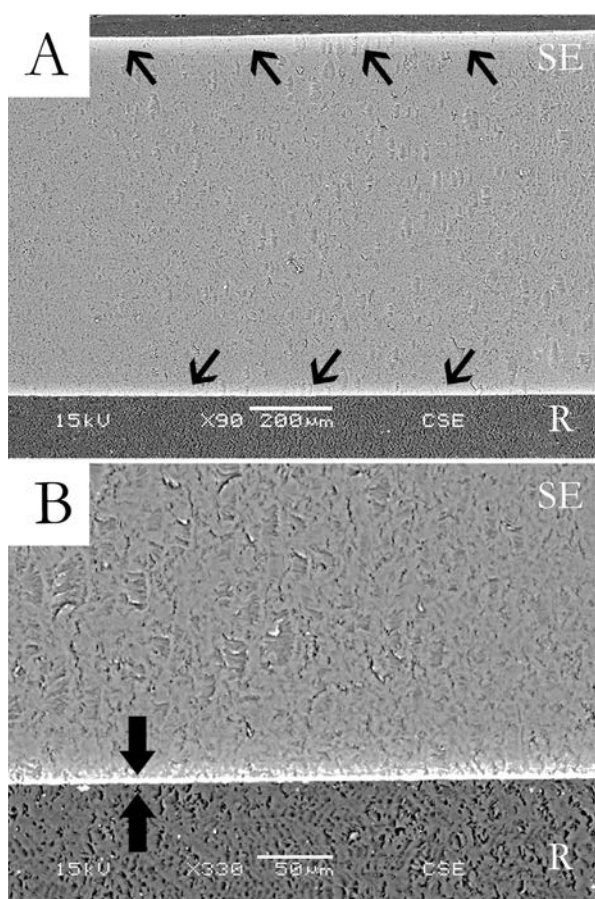


Figure 1. SEM micrographs of a specimen of the bonding resin of Clearfil SE Bond (SE) embedded in epoxy resin (R). (A) At low magnification (90 X), an electronlusc line at the interface of the adhesive-epoxy resin can be seen, indicating that the silver deposition was concentrated in the outer surface of the specimen (narrow arrows). Between the upper and the lower electronlusc lines, no silver infiltration was observed. (B) At higher magnification (330 X), it is confirmed that the silver impregnation was practically restricted to the outer portion of the specimen (between large arrows).

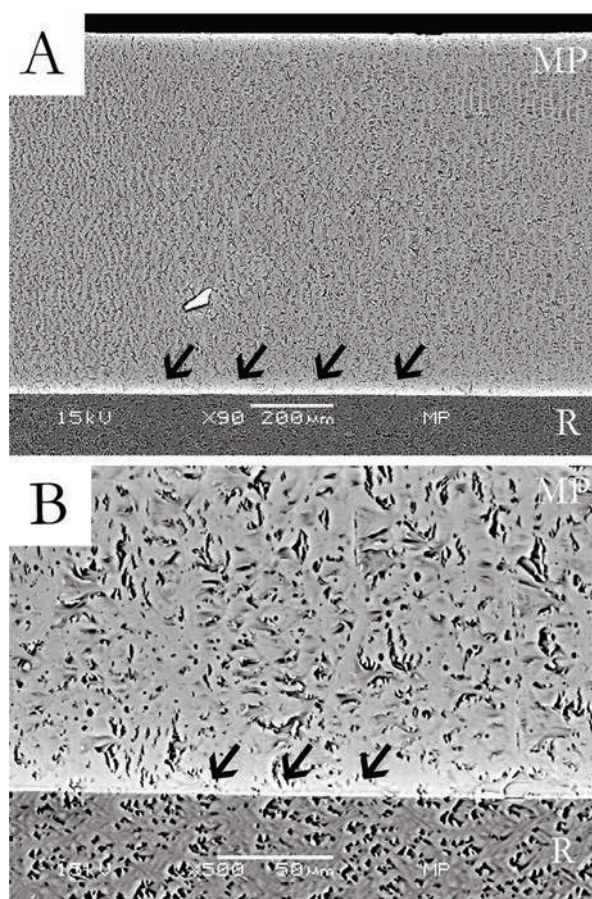


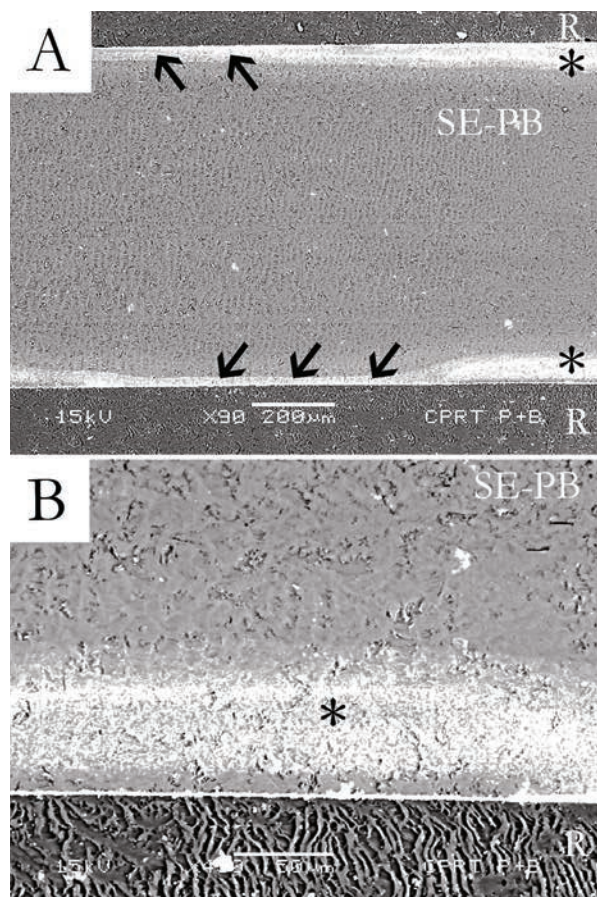
Figure 2. SEM micrographs of a specimen of the bonding resin of Scotchbond Multi-Purpose System (MP). (A) At the lowest magnification (90 X), deposits of silver showed as being restricted to the interface adhesive-epoxy resin (narrow arrows). (B) Even at higher magnification (500 X), it can be observed that silver infiltration was practically restricted to the outer portion of the specimen (narrow arrows).

Table 1. Materials employed in the study and main composition\*.

| Adhesive                                     | Components   | % by Wt | Manufacturer                               |
|--|--|---------|--|
| Clearfil SE Bond (SE; SE-PB)                 | Primer: MDP, HEMA, hydrophilic dimethacrylates, N,N-diethanol p-toluidine, CQ, water<br>Bond: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylates, silanated colloidal silica, N,N-diethanol p-toluidine, CQ | N/E     | Kuraray Co., Osaka, Japan                  |
| Adper Scotchbond Multi-Purpose Adhesive (MP) | HEMA   | 30 - 40 | 3M ESPE Dental Products, St. Paul, MN USA  |
|  | Bis-GMA  | 60 - 70 |  |
|  | Catalysts  | N/E     |  |
| Adper Single Bond 2 (SB)                     | Bis-GMA  | 10 - 20 | 3M ESPE Dental Products, St. Paul, MN USA  |
|  | HEMA   | 5 - 15  |  |
|  | Copolymer of acrylic and itaconic acids  | 5 - 10  |  |
|  | Glycerol 1,3-dimethacrylate  | 5 - 10  |  |
|  | Diurethane dimethacrylate  | 1 - 5   |  |
|  | Silane treated silica  | 10 - 20 |  |
|  | Ethyl alcohol  | 25 - 35 |  |
| Excite (EX)                                  | Phosphonic acid acrylate   | < 11    | Ivoclar Vivadent AG, Schaan, Liechtenstein |
|  | HEMA   | < 15    |  |
|  | Mixture of dimethacrylates   | < 53    |  |
|  | Alcohol  | < 20    |  |
|  | Silicon dioxide  | N/E     |  |
|  | Initiators and stabilizers   | N/E     |  |
| One-Step Plus (OS)                           | HEMA   | 10 - 40 | Bisco, Inc. Schaumburg, IL, USA            |
|  | BPDM, Bis-GMA  | 10 - 40 |  |
|  | Acetone  | 40 - 70 |  |
|  | Dental Glass   | 1 - 10  |  |
| Adper Prompt (AP)                            | Part A: Di-HEMA phosphate  | 75 - 90 | 3M ESPE Dental Products, St. Paul, MN USA  |
|  | Bis-GMA  | 10 - 15 |  |
|  | Ethyl 4-Dimethyl aminobenzoate   | < 2     |  |
|  | DL-CQ  | 1 - 1.5 |  |
|  | Part B: HEMA   | 17 - 28 |  |
|  | Water  | 70 - 90 |  |
| One-Up Bond F Plus (OU)                      | Bonding agent A: MAC-10  | 10 - 30 | Tokuyama Dental Corp., Tokyo, Japan        |
|  | Metacryloyloxyalkyl acid phosphate   | 30 - 60 |  |
|  | MMA  | 5 - 20  |  |
|  | Bisphenol A polyethoxy methacrylate  | 20 - 40 |  |
|  | Bonding agent B: HEMA  | 30 - 60 |  |
|  | MMA  | 10 - 30 |  |
|  | Fluoroaluminosilicate glass filler   | 15 - 30 |  |
|  | Borate catalyst  | < 5     |  |
|  | Water  | 5 - 20  |  |

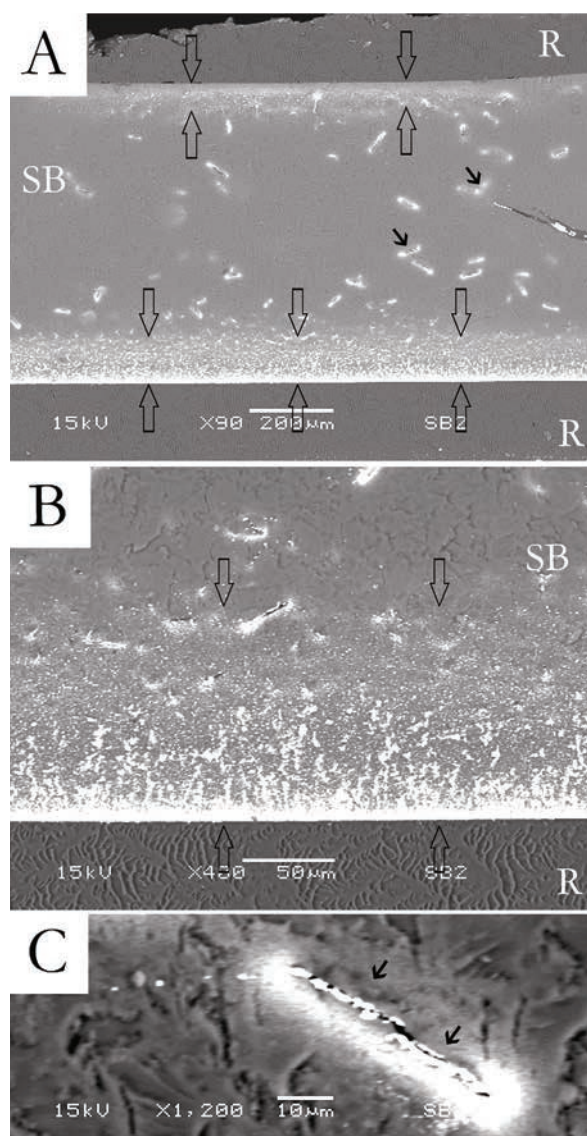
Abbreviations: Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; MDP: 10-methacryloyloxydecyl-dihydrogen phosphate; BPDM: Biphenyl dimethacrylate; MMA: methyl methacrylate; MAC-10: methacryloyloxydecamethylene malonic acid; CQ: camphorquinone; N/E: not disclosed by manufacturers. \*: Basic composition based on the Material Safety Data Sheet research.

less sensitive and simpler to apply. To make adhesives able to demineralize, infiltrate and bond with dentin in fewer steps, hydrophilic monomer and organic solvent contents have been increased in the formulation of adhesives. Hence, it is not surprising that the most simplified systems tested in this study (AP and OU), the so-called “all-in-one” adhesives, exhibited a higher amount of silver deposits than the adhesives SB, EX, and OS, which represent the two-step “etch-and-rinse” adhesives. Conversely, the bonding agents of the systems SE and MP, which are composed of more hydrophobic comonomers (i.e., Bis-GMA), exhibited significantly lower depositions of silver, which were restricted to the specimen’s surfaces. Therefore, the hypothesis that there is no difference in permeability to silver nitrate solution among the tested adhesives cannot be accepted.



**Figure 3.** SEM micrographs of a specimen obtained with the mixture of the primer and the bond components of the Clearfil SE Bond system (SE-PB). (A) At low magnification (90 X), it appears that the deposits of silver were restricted to the 50-μm outer surface of the specimen, in contact with the epoxy resin (narrow arrows). (B) However, at higher magnification (400 X), a multi-phase material can be seen; whereas in the center of the specimen the silver is sparsely deposited, its periphery is densely impregnated (\*) by a foggy line that extends along the interface of the adhesive-epoxy resin. Such phase variability denotes that the primer and the bond components of the Clearfil SE system did not mix well. R-epoxy resin.

As silver particles are carried through polymers while dissolved in water, silver tracer penetration within polymerized adhesives may be interpreted as a visual exhibition of the water diffusion process. Thus, factors related to the increased water sorption in these adhesive systems may also explain the greater silver permeation and deposition. Water sorption into polymer networks is predominantly controlled by two main factors: resin polarity, which is dictated by the concentration of polymer polar sites available to form hydrogen bonds with water,<sup>22,23</sup> and network



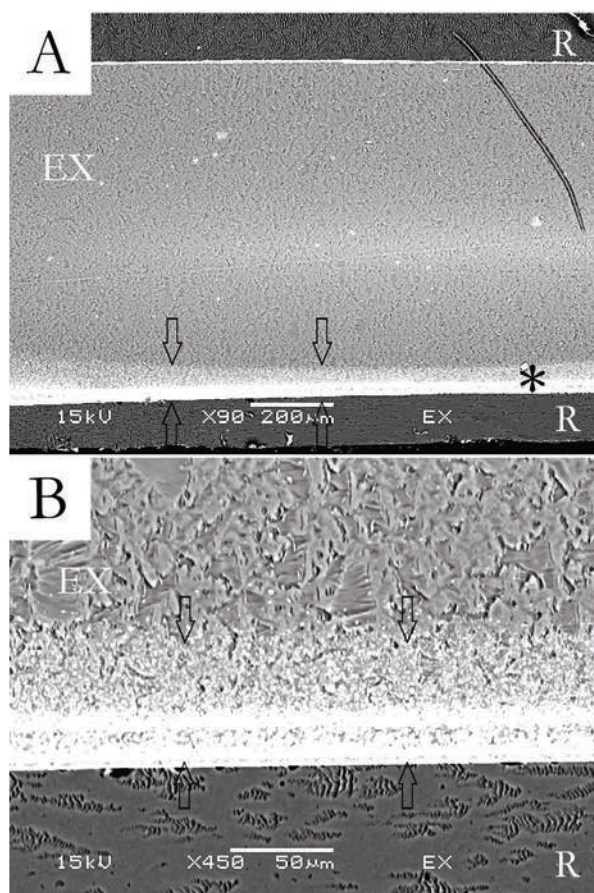
**Figure 4.** SEM micrographs of a specimen of the adhesive Single Bond 2 (SB). (A) At low magnification (90 X), two patterns of silver infiltration can be identified: a granular deposition localized in the outer portions (upper and lower) of the specimen that extends to its center (large unfilled arrows); and a reticular impregnation in the center of the specimen, forming thin, elongated structures (black arrows). (B) Higher magnification (400 X) of the area shows that it is impregnated with the granular pattern of silver deposition (large unfilled arrows). (C) Higher magnification (1,200 X) of the area wherein the silver impregnation formed shows elongated structures (black arrows). R- epoxy resin.

topology, which is related to the density of the polymer network.<sup>22,24,25</sup> Thus, water may diffuse freely through polymers' nanoporosities as "unbound" water or it may diffuse tightly attached to polar domains via hydrogen bonding.

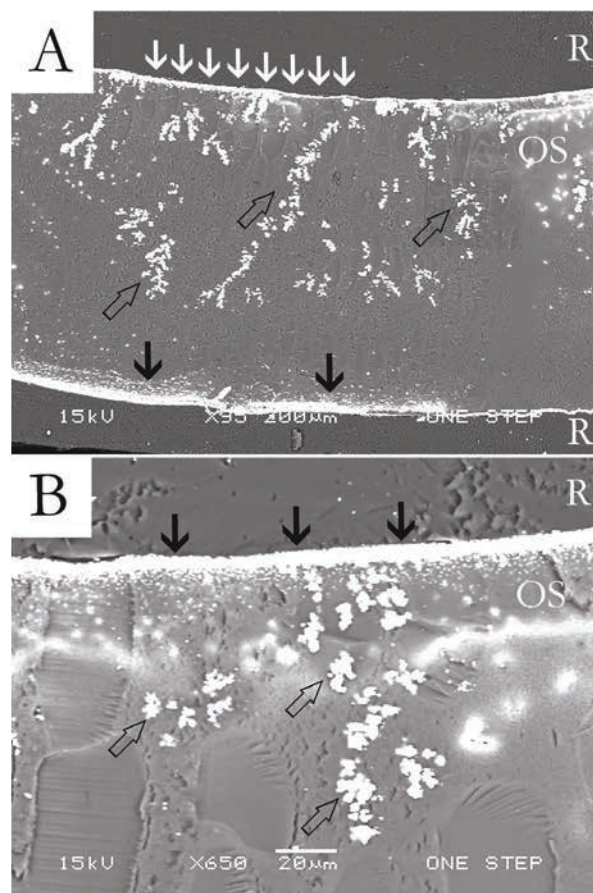
According to the "free volume theory," water can diffuse freely inside the polymer network as unbound water that fills its free volume (pores).<sup>26</sup> On the other hand, the "interaction theory" defends the idea that water can also diffuse as "bound" water that tends to disrupt interchain hydrogen bondings, inducing swelling and thus the opening of additional interchain spaces.<sup>27,28</sup> Thus, as the percentage of relatively hydrophilic monomers (i.e., HEMA, BPDM, PENTA) increases in the adhesive blend, more sites for hydrogen bonding become available for "bound" water diffusion. For consequence, higher opening of additional free

volume by swelling occur with high hydrophilic polymers as longer is the time they stay immersed in a fluid solution.<sup>29</sup> This could explain the intense silver deposition and the inner penetration of ions in materials that are more hydrophilic.

In addition to methacrylate monomers, primers and simplified adhesives also contain water and/or organic solvents. Researchers have observed that the addition of volatile solvents to adhesive formulations implies greater water sorption in the polymerized resin,<sup>30</sup> and this corresponds with the results obtained in this study. In fact, the extension of silver deposition into SB, EX, and OS specimens increased if there was more solvent present in their composition, i.e., 25-35%wt, < 20%wt and 40-70%wt, respectively (Table 1). Although a protocol to aid solvent evaporation had been performed, it is known that complete solvent elimina-



**Figure 5.** SEM micrographs of a specimen of the adhesive Excite (EX). (A) At low magnification (90 X), a dense granular pattern of permeation (large arrows) can be observed at the interface with adhesive-epoxy resin (R). (\*). (B) A higher magnification (450 X) of the area designated with \* shows a granular deposition of silver along the outer 70- $\mu$ m of the specimen (large unfilled arrows).



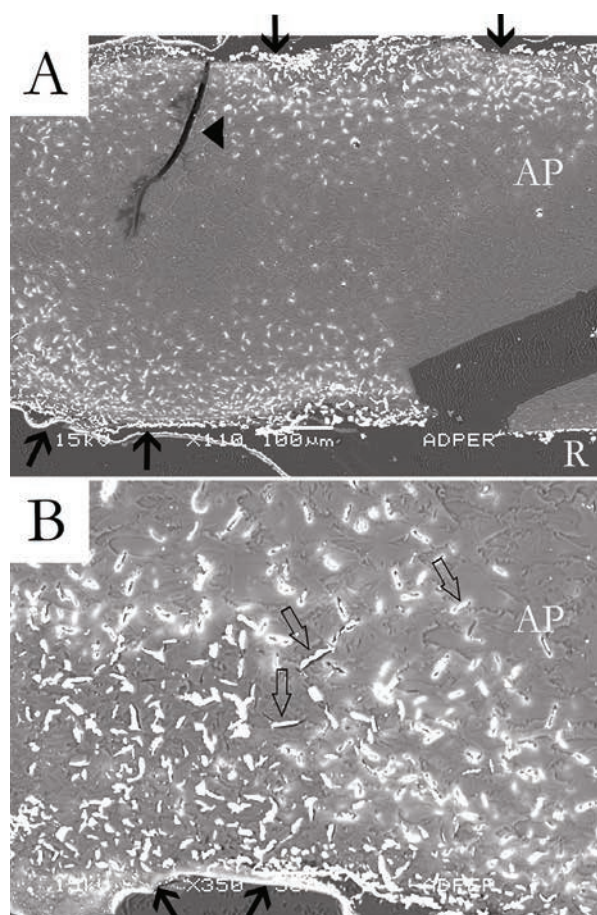
**Figure 6.** SEM micrographs of a specimen of the One-Step adhesive (OS). (A) At low magnification (95 X), an intense silver impregnation can be observed all over the specimen (narrow black arrows and large unfilled arrows). At the interface with adhesive-epoxy resin and extending a few microns toward the center of the specimen a granular pattern of deposition is observed (narrow black arrows). A reticular pattern of deposition (large unfilled arrows) can be observed extending through almost the entire thickness of the specimen. The bent surface (narrow white arrows) indicates that the specimen deformed when it was left to dry. (B) A higher magnification (650 X) of areas impregnated with both granular and reticular silver depositions (narrow black arrows and large unfilled arrows). R - epoxy resin.

tion is difficult, if not impossible, especially from high hydrophilic blends.<sup>31-33</sup> Therefore, residual volatile solvents diluted in the liquid adhesive may have prevented the approximation between reactive pendant species, making cross-linking reaction more difficult.<sup>34</sup> Thus, instead of achieving optimal macromolecular packing density, the polymer backbone may have had its free volume greatly augmented to a level directly related to the amount of organic solvent present during polymerization, even though a good degree of conversion was achieved.<sup>34</sup>

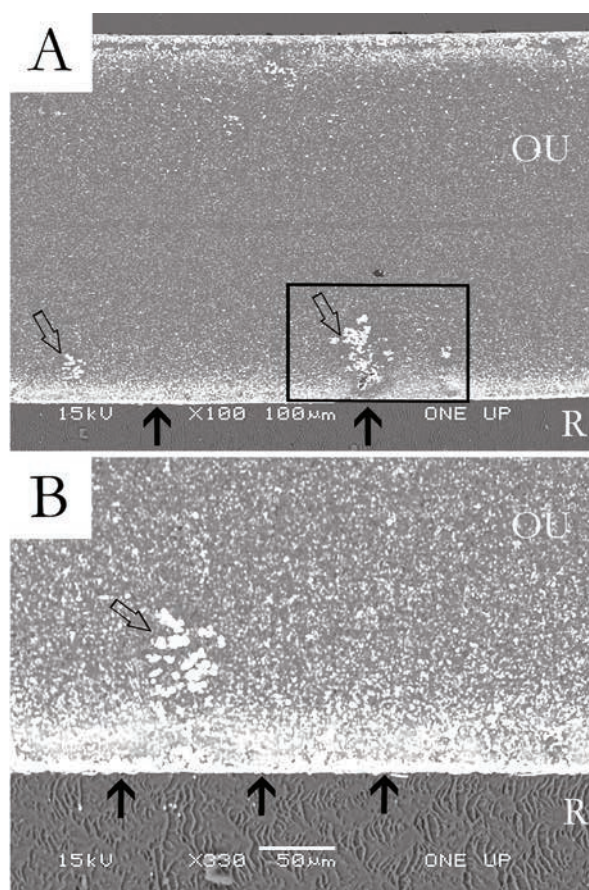
The effect of solvent presence in an adhesive composition seemed to be more marked in OS, the system with the higher concentration of solvent (acetone). Beyond the granular pattern of silver deposition, which is the result of silver precipitation in free space, a reticular pattern of silver precipitation resembling what is known as water-

trees was also observed in OS micrographs. In previous work,<sup>35</sup> a great agitation of molecules was observed during the polymerization of an acetone-solvated resin. Researchers pointed out that such agitation was due to the fast acetone volatilization, which is favored by the increase in temperature, that results from the polymerization reaction, and by acetone's low boiling point (56°C) and high vapor pressure (200 mmHg at 25°C).<sup>35</sup> We speculate that the reticular pattern of infiltration observed in OS occurred due to the great agitation of acetone molecules that could not escape from the specimen because of the presence of the glass slide.

A greater silver deposition, accompanied by several cracks, was observed in AP micrographs. The higher amount of hydrophilic monomers in AP, compared to the other tested materials, could be responsible for the faster and larger uptake of silver<sup>8,36</sup> that ended up permanently damaging the



**Figure 7.** SEM micrographs of a specimen of the adhesive Adper Prompt (AP). (A) At the lowest magnification (110 X), an intense silver deposition can be observed over the entire thickness of the specimen. Irregular margins represent the distortion that occurred in the specimen during storage in the tracer solution (narrow arrows). A crack is observed emerging from the specimen (◄). (B) At a higher magnification (350 X), one can see that the silver deposition occurred predominantly in the form of thin, elongated structures (large unfilled arrows), similar to the ones observed in the SB specimens (Fig. 4). R - epoxy resin.



**Figure 8.** SEM micrographs of a specimen of the adhesive One-Up bond F (OU). (A) At low magnification (100 X), a granular deposition occupies much of the outer surfaces (upper and lower) (narrow black arrows), becoming more sparse in the center of the specimen. A reticular silver deposition was also observed, but it was restricted to a few areas (large unfilled arrows). (B) A higher magnification (330 X) of the area limited with a rectangle in A. R - epoxy resin.



polymer structure. Moreover, the increased concentration of water in AP, in conjunction with incompatibilities between co-initiators and the very acidic and hydrophilic phase, could have rendered lower monomer polymerization, determining the formation of a loosely compact polymer that is prone to rapidly absorb water/silver.<sup>37-39</sup> One could argue that the polymerization of AP and OU the self-etching adhesives evaluated in this study inside a mold could have interfered with their optimal polymerization and, as a consequence, have led to a greater permeability of these materials. The idea that the acidity of these simplified adhesives is neutralized when they are applied to dentin due to a reaction with hydroxiapatite crystals, favor the belief that the degree of conversion of such materials would be improved under such condition. However, previous studies on polymerization of self-etching adhesives have shown that they can achieve a similar degree of conversion when polymerized in a mold for an extended period (91% after 60 s of irradiation)<sup>40</sup> or when they are applied on dentin (79% - 93%).<sup>41</sup> Accordingly, the photoactivation time employed in this study (80 s) would have been enough to produce a comparable and clinically relevant degree of conversion to that produced when these materials are polymerized on dentin. The increased permeability found in the one-step, self-etching adhesives evaluated in this study is in accordance with the results of increased water diffusion through dentin interfaces bonded to similar simplified adhesives, even though, in the former study, they had been extensively photo-activated prior to the testing of their permeability.<sup>40</sup>

Apart from the differences in the amount of silver deposited, which were found to be greatly related to the material's hydrophilicity,<sup>36</sup> this study identified differences in the pattern and in the specific location of silver deposition over the superficies analyzed. It is worth noting that all adhesives evaluated depicted silver permeation only or mostly along the interface with the epoxy resin, i.e., in the superficies of the specimen, though everyone had been produced in confinement, inside a mold, covered with a glass slide in an attempt to exclude oxygen inhibition layer in the superficies.<sup>42-44</sup> Thus, a different location of a silver deposition might be explained only by the non-homogeneity of polymerization in the bulk of specimens<sup>35</sup> due to phase

separation of very different elements.<sup>45</sup> Volatile solvents and hydrophilic monomers with a low molecular weight might have concentrated near the adhesive surface, causing lower monomer polymerization in this area.<sup>34,35</sup> Consequently, differences in the quality of polymerization through the specimen determined the spatial anisotropy of the cured polymer, and, finally, the spatial distribution of silver particles.

Strong evidence of phase separation was specifically observed in SE-PB specimens. Although we were careful to achieve a proper mixture of the primer and the bond components of the adhesive system, the micrographs depicted two very distinct phases over the specimens - one deficiently and another greatly infiltrated by silver particles. Such a great difference leads us to speculate that primer and bond liquids do not mix properly. Chemical incompatibilities between these two liquids could be responsible for their non-miscibility. The self-etching primer applied in this study is basically a mixture of hydrophilic monomers, solvated in water. In contrast, the bond component of the system is composed of a great quantity of hydrophobic monomers, which are not miscible with water.<sup>45</sup> The reduced miscibility of the primer and the adhesive can therefore determine the maintenance of two different phases slightly attached by very hydrophilic and weak linkages.

This study's results showed that a great number of silver ions were able to diffuse through simplified, more hydrophilic adhesives, even though they were polymerized over an inert, water-free substrate, i.e., a brass mold. Additionally, a great silver diffusion was observed through the primer of a multi-step adhesive system. Thus, despite being clinically more stable,<sup>10</sup> the three-step etch-and-rinse adhesives and two-step self-etch systems may also produce degradable bonded interfaces limited by the stability of their bond agents over the instability of their primers.<sup>46</sup> Therefore, future research should be done to clinically bond hydrophobic materials to dental tissues.

## CONCLUSIONS

Within the limits of the present study, it can be concluded that simplified, hydrophilic adhesives allow higher fluid diffusion than less hydrophilic ones that must be applied to dentin in multiple steps. High fluid diffusion can be related to the

higher solvent and hydrophilic monomer content in a simplified adhesive's composition and to the high acidity of one-step, self-etching adhesives.

Even in multi-step adhesives, fluid diffusion can be relevant, due to the great permeability observed through the very hydrophilic and solvated primer component.

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