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Influence of Water-storage Time on the Sorption and Solubility Behavior of Current Adhesives and Primer/Adhesive Mixtures

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Clinical Relevance

The simplified one-step self-etching adhesive and primer/adhesive blends presented high water sorption values that increased with increased water-storage time. High water sorption and solubility values might be related to marginal discoloration and degradation of the bond.

SUMMARY

This study evaluated the effects of water-storage on the water sorption and solubility behavior of five commercially available dental adhesive systems and two primer/adhesive mixtures. The adhesives comprised three different approaches to bonding to hard tooth tissues: a one-step self-etching adhesive (One-up Bond F), two two-step self-etching primers (Clearfil SE Bond and Clearfil Protect Bond) and two etch-and-rinse systems: a water/ethanol-based (Single Bond) and an acetone-based filled adhesive (Prime&Bond NT). The bonding agents and primers of the two-step self-etching systems were mixed in a 1:1 volume ratio. Water sorption and solubility values were determined after 1, 7, 30, 90 and 180 days. The results showed that, except for SB, all adhesives presented increased water sorption with increased storage time. The one-step self-etching adhesive and self-etching primer/adhesive mixtures presented the highest water sorption and solubility values. Equilibrium in the water sorption values was observed for all adhesives after 90 days of water-storage. However, solubility values continued to increase for some materials until 180 days. The sorption and solubility behavior of the materials tested seem to be related to hydrophilicity of the adhesive resin solution and might influence the long-term performance of resin-based composite restorations.

INTRODUCTION

One of the major concerns in adhesive dentistry is the durability of bonds to dentin substrate, because bonding is established on a complex hydrated biological composite structure.[1-2] Adhesive systems are hydrophilic in nature, because hydrophilicity is desirable for bonding

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to a moist substrate such as dentin. However, subsequent water sorption within bonded interfaces is thought to contribute to degradation over time.[3-4]

Adhesive dentistry has been facing a trend towards simplification of bonding procedures. Different approaches, with different numbers of steps and degrees of sensitivity, have been used to bond resin-based materials to enamel and dentin.[5-7] However, simplification of bonding procedures has resulted in increased hydrophilicity and, consequently, decreased long-term bonding effectiveness.[8] One-bottle self-priming etch-and-rinse systems and single-step self-etching adhesives are more hydrophilic versions of their multiple-step precursors.[7-8] The incorporation of increased concentrations of hydrophilic monomers into adhesive systems may compromise bond durability, as hydrophilicity and hydrolytic stability are antagonistic properties.[9]

It is well known that bond strength and quality of the seal produced by bonding agents decrease with time both *in vitro* and *in vivo*.[4,10-12] Water sorption within resin-dentin interfaces has been quoted as one of the dominant factors involved in adhesion degradation.[3] However, while numerous studies have examined the water sorption and solubility behavior of restorative resin composites, data on the water sorption and solubility characteristics of adhesive systems currently available in the market and their influence in bond longevity is scarce.[13-14] This study evaluated the water sorption and solubility characteristics of five adhesive systems and two primer/adhesive mixtures over a 180-day water-storage period. The null hypotheses tested were: (1) different adhesive solutions present no significant difference in water sorption and solubility behavior and (2) increased water-storage time does not affect the water sorption and solubility behavior of the materials tested.

METHODS AND MATERIALS

Specimen Preparation

Five adhesive systems were used in this study. These systems comprised three categories: one single-step self-etching adhesive (One-up Bond F [OB], Tokuyama, Tokyo, Japan), two two-step self-etching primers (Clearfil SE Bond [CF] and an antibacterial fluoride-containing system, Clearfil Protect Bond [CP], Kuraray Medical Inc, Tokyo, Japan) and two two-step etch-and-rinse adhesives: a water/ethanol-based (Single Bod [SB], 3M ESPE, St Paul, MN, USA) and an acetone-based filled adhesive (Prime&Bond NT [PB], Dentsply/Caulk, Milford, DE, USA). In addition, two primer/adhesive mixtures were tested. The self-etching primers (P) were mixed with the respective hydrophobic bonding agents of Clearfil SE Bond (CF) and Clearfil Protect Bond (CP) in a 1:1 volume ratio (CF+P and CP+P). A 1:1 primer/adhesive volume ratio was used, because it can provide insight into how the water sorption and solubility behavior might be affected within the resin-tooth interface produced with the self-etching primer systems when primer and adhesive solutions are mixed. Composition, batch number and manufacturers of each adhesive system are listed in Table 1.

All the adhesive systems tested present a certain amount of solvents and water in their composition, which could impair polymerization of specimens. Thus, the authors of this study tried to eliminate or at least reduce their content in the adhesive solutions of SB, PB, CP and CF primers. No attempt to reduce the presence of solvent in OB was done, because the manufacturer's instructions do not recommend air-drying after application. For solvent elimination, several drops of each adhesive or primer were dispensed in an adhesive dispenser, and the solution mass was recorded on an analytical balance (JEX-200, YMC Co Ltd, Kyoto, Japan) until reaching equilibrium at room temperature.[15] The amount of time necessary for each adhesive system to reach a constant mass was determined. Solvent evaporation was done in a dark box to prevent early polymerization of the adhesives. Glass pipettes were then used to fill a hollow cylinder of approximately 12 mm that was cut from micro bore tygon tubing (TYG-030, Small Parts Inc, Miami Lakes, FL, USA) with an internal diameter of approximately 0.73 mm. A light curing unit (Astralis 5, Ivoclar Vivadent, Schaan, Liechtenstein) with an output of 650 mW/cm^2 was used to photo-activate specimens for 120 seconds. A razor blade was then used to section the cylinders into 2 mm high cylinders. The specimens were carefully removed from the tygon tubing and randomly assigned to each of the storage periods in water (n=5): 1, 7, 30, 90 and 180 days.

Sorption and Solubility Analysis

A micro-balance (Sartorius 142P, Goettingen, Germany) with a precision of 0.001 mg was used for weighing the specimens. The water sorption/solubility test was performed according to ISO 4049 (1988) for resin-based filling materials, with the exception that the specimens were weighed shortly after preparation (m_1 was recorded. The specimens were then stored for 24 hours) and the dimensions of the specimens were reduced in relation to the original standard. The specimens were immersed individually in an eppendorf container with 1.5 ml of distilled water at 37°C for each storage period. After completing the storage periods (1, 7, 30, 90 or 180 days), the specimens were removed from water, any visible moisture was removed with a paper towel and 1 minute after removal from water mass m_2 was recorded. The specimens were then stored for 24 hours in a desiccator containing freshly dried silica gel and a constant mass (m_3) was obtained. The diameter and thickness of the specimens were measured at three different points using a digital caliper with a precision of 0.01 mm (Mitutoyo, Tokyo, Japan) and the volume (V) was calculated in cubic millimeters. The values of water sorption (W_{sp}) and solubility (W_{sl}) were measured and calculated using the following formula:

$$W_{sp} = (m_2-m_3)/V \qquad W_{sl} = (m_1-m_3)/V$$

where:

m_1 is the mass of the specimen in micrograms before immersion in water;

m_2 is the mass of the specimen in micrograms after immersion in water;

m_3 is the mass of the specimen in micrograms after desiccation and

V is the specimen volume in cubic millimeters.

Statistical Analysis

Differences in water sorption and solubility values were statistically evaluated using two-way ANOVA (adhesive vs storage time) and the Tukey post-hoc test at a pre-set significance level of 0.05. Statistical analyses were done using SAS for Windows (V8, SAS Institute, Cary, NC, USA).

RESULTS

Results for the water sorption and solubility tests are presented in Tables 2 and 3, respectively. Figure 1 graphically demonstrates water sorption and solubility behavior for the adhesive systems and primer/adhesive mixtures after storage in water. Two-way ANOVA revealed that there were statistically significant differences for the factor "adhesive" ($p \leq 0.0001$) and "storage time" ($p \leq 0.0001$), and it identified a significant interaction between factors ($p \leq 0.0001$). The above information is valid for both analyses (sorption and solubility). The Tukey post-hoc test showed significant differences among adhesive systems at different storage times ($p<0.05$).

Water sorption analysis revealed that tested groups present significantly different water sorption patterns and a different behavior after storage in water (Table 2). PB presented the lowest sorption values, followed respectively by CF, CP, SB and CF+P and CP+P and OB. Except for CP+P and OB, significant differences were observed among adhesives at all periods tested. Similar values were also observed between CF+P and CP+P after 180 days of storage in water. Except for SB, all groups presented a significant increase in water sorption values with increased water-storage time.

Table 1: *Materials, Brand (Lot #), Composition, Application Technique and Manufacturers of Adhesive Systems Used in This Study*

Material	Brand (Lot #)	Code	Composition	Manufacturer
2-step Self-etching Primers	Clearfil Protect Bond (primer: 00002A bond: 00004A)	CP	*Primer*: MDP, HEMA, MDPB, dimethacrylates, photoinitiator, water *Adhesive*: MDP, HEMA, photoinitiator, NaF, silanated colloidal silica	Kuraray Medical Inc, Tokyo, Japan
	Clearfil SE Bond (primer: 00400A bond: 00541A)	CF	*Primer*: Water, ethanol, MDP, HEMA, dimethacrylate hydrophilic, canphorquinone, N, N-diethanol p-toluidine silanated colloidal silica	Kuraray Medical Inc, Tokyo, Japan
1-step Self-etching Adhesive	One-up Bond F (Bonding A: 084 Bonding B: 578)	OB	Water, MMA, HEMA, coumarin dye, metacryloyloxyalkyl acid phosphate, MAC-10, multifunctional methacrilic monomer, fluoraluminosilicate glass, photoinitiator (aryl borate catalyst)	Tokuyama Corp, Tokyo, Japan
2-step Total-etch Adhesives	Prime&Bond NT (030822)	PB	*Etchant*: 35% H_3PO_4 *Adhesive*: PENTA, UDMA, resin R5-62-1, resin T, resin D, silica nanoparticles, photoinitiators, cetilamine hidrofluoride and acetone	Dentsply Caulk, Milford, DE, USA
	Single Bond (3JL)	SB	*Etchant*: 35% H_3PO_4 *Adhesive*: water, ethanol, Bis-GMA, HEMA, UDMA, Bisphenol A glycerolate, polyalkenoic acid copolymer, dimethacrylate, canphorquinone	3M ESPE, St Paul, MN, USA

MDP, 10-methacryloyloxydecyl dihydrogen phosphate; HEMA, 2-hydroxyethyl methacrylate; MDPB, 12-methacryloyloxydodecylpyridinium bromide; MMA, methyl methacrylate; MAC-10, methacryloyloxydecamethilene malonic acid; PENTA, dipentaerythritol pentacrylate phosphoric acid ester; UDMA, urethane dimethacrylate; Bis-GMA, bisphenol-A diglycidil ether dimethacrylate.

Stability in water sorption values was only observed after 90 days of immersion in water for the other groups. The primer/adhesive mixtures (CF+P and CP+P) and the single-step self-etching adhesive OB absorbed considerably more water than the other groups.

A tendency towards increased solubility was observed with increased storage time for all groups (Table 3, Figure 1). The primer-adhesive mixture CF+P and the single-step adhesive OB presented the highest solubility values. On the other hand, CP presented the lowest values over the course of the experiment. Solubility increased significantly for all materials tested. After 180 days, the solubility values of all materials were at least two times higher than values observed after one day storage in water.

DISCUSSION

Bonding to a vital, wet substrate such as dentin has been proven to be a difficult task. The mineral phase of the substrate needs to be totally or partially removed and substituted with an adhesive solution that will permeate this collagen-rich layer and polymerize *in situ*, forming the hybrid layer.[16] Adhesive systems are largely exposed to dentinal fluids and, to a lesser extent, to salivary fluids in the oral environment. The water sorption and solubility characteristics of adhesive materials are important in determining the longevity and marginal quality of a restoration. High water sorption values might contribute to marginal staining around composite restorations.[13] Water plays an important role in the chemical degradation process of polymer materials.[17-18] Thus, more hydrophobic materials tend to take up lower quantities of water and, consequently, present a lower hydrolytic degradation velocity.

Two different theories, which are believed to occur simultaneously, have been proposed related to the diffusion of water molecules into polymer matrices. In the "free volume theory," water molecules diffuse through nanopores or micromorphological defects of the materi-

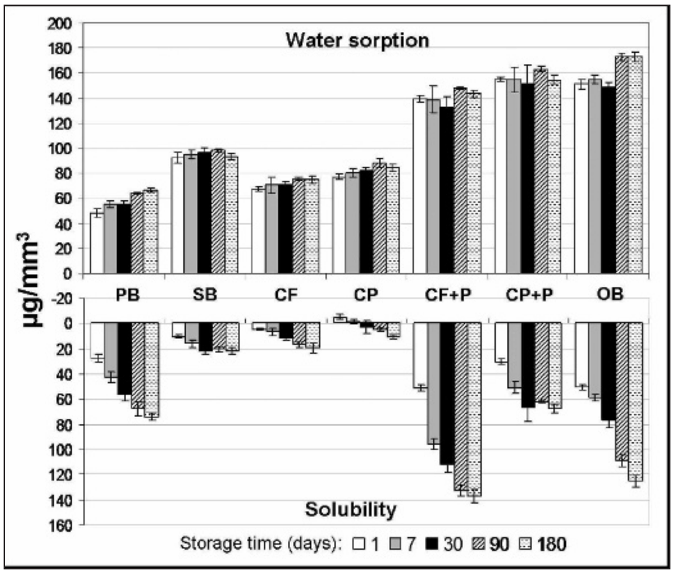

Figure 1. *Mean values and standard deviation for water sorption and water solubility (µg/mm³) of the adhesive materials tested after 1, 7, 30, 90 and 180 days of water storage.*

Table 2: *Mean Values and Standard Deviation for Water Sorption (µg/mm³) of the Adhesive Materials Tested After 1,7,30,90 and 180 Days of Water Storage*

	1 Day		7 Days		30 Days		90 Days		180 days	
Prime&Bond NT	48.07 ± 3.25	Fc	55.12 ± 2.39	Fb	55.33 ± 2.26	Fb	63.81 ± 0.73	Fa	66.51 ± 2.02	Fa
Single Bond	92.32 ± 4.15	Ca	94.82 ± 3.19	Ca	96.89 ± 2.89	Ca	98.01 ± 1.25	Ca	93.12 ± 2.77	Ca
Clearfil SE Bond	67.33 ± 1.45	Eb	70.33 ± 6.22	Eab	70.99 ± 2.26	Eab	75.35 ± 1.60	Ea	74.73 ± 2.94	Ea
Clearfil Protect Bond	77.01 ± 2.27	Dc	80.02 ± 3.40	Dbc	82.21 ± 2.01	Dabc	87.89 ± 3.10	Da	84.20 ± 2.85	Dab
C SE Bond + primer	139.56 ± 2.82	Bab	138.99 ± 10.74	Bab	132.59 ± 8.84	Bb	148.15 ± 1.15	Ba	143.58 ± 3.38	Ba
C Protect Bond + primer	155.23 ± 2.03	Aab	154.89 ± 9.82	Aab	151.49 ± 14.67	Ab	163.30 ± 2.21	Aa	154.69 ± 3.87	Bab
One-up Bond F	151.35 ± 4.05	Ab	155.11 ± 3.44	Ab	149.51 ± 2.88	Ab	172.98 ± 2.94	Aa	172.95 ± 3.88	Aa

Means followed by different letters (capital–column, lower case–row) differ among them by Tukey test at the 0.05 confidence level.

Table 3: *Mean Values and Standard Deviation for Water Solubility (µg/mm³) of the Adhesive Materials Tested After 1,7,30,90 and 180 Days of Water Storage*

	1 Day		7 Days		30 Days		90 Days		180 days
Prime&Bond NT	27.77 ± 2.97	Bd	42.40 ± 4.28	Dc	56.07 ± 5.51	Db	67.82 ± 5.53	Ca	74.25 ± 3.00
Single Bond	10.58 ± 1.49	Cb	16.31 ± 3.10	Eab	22.01 ± 2.51	Ea	20.59 ± 2.19	Da	22.01 ± 2.45
Clearfil SE Bond	4.83 ± 1.03	Cc	6.58 ± 3.01	Fbc	11.30 ± 2.25	Fbc	16.53 ± 2.56	Dab	19.76 ± 3.79
Clearfil Protect Bond	-4.95 ± 2.09	Dc	-1.23 ± 1.60	Gbc	3.07 ± 5.42	Gb	4.71 ± 1.85	Eb	12.26 ± 1.90
C SE Bond + primer	51.40 ± 2.49	Ad	95.40 ± 4.22	Ac	112.27 ± 6.06	Ab	132.29 ± 4.18	Aa	137.16 ± 5.04
C Protect Bond + primer	30.21 ± 2.33	Bc	50.83 ± 4.50	Cb	66.30 ± 11.40	Ca	62.15 ± 1.42	Ca	67.35 ± 3.28
One-up Bond F	50.56 ± 2.32	Ae	58.62 ± 2.48	Bd	76.72 ± 6.13	Bc	108.92 ± 4.41	Bb	125.18 ± 4.64

Means followed by different letters (capital–column, lower case–row) differ among them by Tukey test at the 0.05 confidence level.

al without mutual relationship to the polar sites of the material. In the "interaction theory," water molecules diffuse through the material, binding successively to the hydrophilic groups.[19] There are several factors involved in polymer water sorption and solubility characteristics, such as pH of the storage media;[20-21] degree of conversion,[22] polarity of the molecular structure, presence of pendant hydroxyl groups capable of forming hydrogen bonds with water, degree of crosslinking,[23] presence of residual water and presence and type of filler particles.[14,24-25] After entering the polymer matrix, water triggers chemical degradation, resulting in the formation of oligomers and monomers.[17] The microstructure might be changed due to progressive degradation through the formation of pores. Residual monomers, oligomers and degradation products might be released via these pores.[17,26-27] In addition to the degradation process within the polymer, debonding between the polymer and filler particles might occur, resulting in leakage of the filler particles and ions. The degradation and erosion process leads to a mass loss of the adhesive material measured as solubility.

The adhesive materials tested in this experiment present different amounts of hydrophilic and hydrophobic monomers in their composition. Water and solvents are also present in the adhesive blend. In order to bond to the intrinsically wet dentin surface, adhesive systems incorporate resin molecules with both hydrophilic and hydrophobic moieties, or hydrophilic resins, such as 2-hydroxyethylmethacrylate (HEMA). The self-etching ability of contemporary adhesives is commonly achieved by incorporating polymerizable, methacrylate-based resin monomers that contain carboxylic/phosphoric acid moieties or their esters or by incorporating mineral or organic acids as additives to non-acidic hydrophilic resin monomers.[6,28] The presence of water is also an essential component, in order to enable ionization of acidic monomers and demineralization of underlying enamel and/or dentin.[6] Besides the presence of water in their composition, the ionizable moieties of acidic monomers are hydrophilic. These observations might explain the highest water sorption rates recorded for the self-etching adhesive OB and the self-etching primer/adhesive blends (CF+P and CP+P) tested in this study. High solubility values were also observed for these groups. The primer/adhesive volume ratio (1:1) was certainly higher than it would be in actual clinical conditions. During application of the self-etching primer adhesive systems to the tooth surface, primer and adhesive solutions mix to some extent. The actual ratio of each component (primer and adhesive) of the mixture within the adhesive layer cannot be easily determined, as it varies along the resin-tooth interface.[12] Concentration of the self-etching primer tends to be higher closer to the hybrid layer and concentration of the hydrophobic adhesive solution increases as it gets closer to the resin composite.[12] It has been demonstrated that mixtures containing higher amounts of primer present a lower degree of conversion and inferior mechanical properties when compared with mixtures containing a lower proportion of primer.[29] Both null hypotheses were rejected, because different water sorption and solubility rates were observed for the groups tested in this study, and they tended to increase with increased water-storage time.

Except for OB, all filled adhesives (PB, CF and CP) presented lower water sorption rates than unfilled adhesives. The presence of filler might provide the adhesives with improved mechanical properties and decreased water sorption.[24,30] The bonding agents of the two-step self-etching systems proved to be more hydrophobic resins. Low water sorption rates and decreased solubility in water were observed for CP and CF. Even though CF presented lower water sorption means than CP, CP presented the lowest solubility rates over the experiment. The same trend was observed for the primer/adhesive mixtures. CP+P presented higher water sorption rates but lower solubility in water than did CF+P. Moreover, CP also showed a mass increase after one and seven days of storage in water. A possible explanation for the increased mass of CP and the lower water solubility of CP and CP+P is chemical reactions with water within the adhesive and the production of reaction products.[31] An important feature of two-step self-etching systems that might contribute to the better results when compared to one-step systems is the hydrophobic resin layer that is placed over the primer, which might reduce water sorption.[12]

The solvent depleted UDMA/PENTA filled solution of PB presented the lowest water sorption values. However, solubility values were higher than those observed for SB, CF and CP and were comparable to those recorded for CP+P. The low water sorption values are probably due to the presence of nanofillers within the bonding solution. However, even though the fillers, themselves, are relatively inert inorganic materials, the coupling agents associated with them are prone to hydrolysis via ester linkages within the molecules or siloxane links that are formed with the filler particle.[32] The elution of filler particles might have occurred for PB after storage in water.

The materials' compositions are inherently prone to hydrolysis due to the presence of unprotected ester linkages in the monomers.[17] The presence of monomers with different properties, such as molecular weight, hydrophilicity (hydrophobicity) and degradation behavior, might induce preferential degradation of one phase in a polymer system.[33] This could lead to the formation of pores within the polymer matrix. Yiu and others[34] recently reported that the increased hydrophilicity of resin blends, such as those employed in dentin adhesives, resulted in decreased mechanical strength after long-term water storage. Increased water-storage time resulted in increased solubility values for all adhesives tested in this investigation. For SB, stabilization in solubility values was observed after seven days; 30 days for CP+P and 90 days for CF+P, CF and PB. Increased solubility was still observed for CP and OB after 180 days of storage in water. Elution of degradation products might have occurred over the water-storage period. The leaching of monomers has a potential impact on the structural stability and biocompatibility of the material.[35] The reduction of some mechanical properties of resin composites (such as modulus of elasticity, strength and hardness) has been attributed to the plasticizing effect of water.[23] The same plasticization effect can be expected to occur in adhesive systems.[36]

The water sorption and solubility values of bonding agents have been reported to be much higher than composite filling materials.[14] High water sorption and solubility values could lead not only to marginal discoloration, but to decreased mechanical properties of the resin-dentin interface and possibly to compromised restoration longevity. Simplification of clinical application procedures has resulted in a loss of bonding effectiveness.[8,37] High water sorption and solubility rates were observed for the 1-step self-etching adhesive OB and the primer/adhesive blends CP+P and CF+P. Further research is necessary for the promotion of simplified adhesives able to bond to a moist substrate such as dentin, but with more hydrophobic characteristics after polymerization and less susceptibility to water solubility.

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References

1. Marshall GW Jr, Marshall SJ, Kinney JH & Balooch M (1997) The dentin substrate: Structure and properties related to bonding *Journal of Dentistry* **25(6)** 441-458.
2. Tay FR, Hashimoto M, Pashley DH, Peters MC, Lai SC, Yiu CK & Cheong C (2003) Aging affects two modes of nanoleakage expression in bonded dentin *Journal of Dental Research* **82(7)** 537-541.
3. Tanaka J, Ishikawa K, Yatani H, Yamashita A & Suzuki K (1999) Correlation of dentin bond durability with water absorption of bonding layer *Dental Materials Journal* **18(1)** 11-18.
4. Hashimoto M, Ohno H, Kaga M, Endo K, Sano H & Oguchi H (2000) *In vivo* degradation of resin-dentin bonds in humans over 1 to 3 years *Journal of Dental Research* **79(6)** 1385-1391.
5. Kanca J 3rd (1992) Resin bonding to wet substrate. 1. Bonding to dentin *Quintessence International* **23(1)** 39-41.
6. Tay FR & Pashley DH (2001) Aggressiveness of contemporary self-etching systems. I: Depth of penetration beyond dentin smear layers *Dental Materials* **17(4)** 296-308.
7. De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, Lambrechts P & Vanherle G (2003) Four-year water degradation of total-etch adhesives bonded to dentin *Journal of Dental Research* **82(2)** 136-140.
8. De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M & Van Meerbeek B (2005) A critical review of the durability of adhesion to tooth tissue: Methods and results *Journal of Dental Research* **84(2)** 118-132.
9. Tay FR, Pashley DH & Yoshiyama M (2002) Two modes of nanoleakage expression in single-step adhesives *Journal of Dental Research* **81(7)** 472-476.
10. Sano H, Yoshikawa T, Pereira PN, Kanemura N, Morigami M, Tagami J & Pashley DH (1999) Long-term durability of dentin bonds made with a self-etching primer, *in vivo Journal of Dental Research* **78(4)** 906-911.
11. Giannini M, Seixas CA, Reis AF & Pimenta LA (2003) Six-month storage-time evaluation of one-bottle adhesive systems to dentin *Journal of Esthetic and Restorative Dentistry* **15(1)** 43-48.
12. Reis AF, Arrais CA, Novaes PD, Carvalho RM, de Goes MF & Giannini M (2004) Ultramorphological analysis of resin-dentin interfaces produced with water-based single-step and two-step adhesives: Nanoleakage expression *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **71(1)** 90-98.
13. Burrow MF, Inokoshi S & Tagami J (1999) Water sorption of several bonding resins *American Journal of Dentistry* **12(6)** 295-298.
14. Mortier E, Gerdolle DA, Jacquot B & Panighi MM (2004) Importance of water sorption and solubility studies for couple bonding agent—resin-based filling material *Operative Dentistry* **29(6)** 669-676.
15. Reis AF, Oliveira MT, Giannini M, de Goes MF & Rueggeberg FA (2003) The effect of organic solvents on one-bottle adhesives' bond strength to enamel and dentin *Operative Dentistry* **28(6)** 700-706.
16. Nakabayashi N, Kojima K & Masuhara E (1982) The promotion of adhesion by the infiltration of monomers into tooth substrates *Journal of Biomedical Materials Research* **16(3)** 265-273.
17. Göpferich A (1996) Mechanisms of polymer degradation and erosion *Biomaterials* **17(2)** 103-114.
18. Reis AF, Pereira PNR & Giannini M Water-induced nanoleakage prevention by bonding strategies (submitted).
19. Bellenger V, Verdu J & Morel E (1989) Structure-properties relationships for densely cross-linked epoxy-amine systems based on epoxide or amine mixtures *Journal of Materials Science* **24(1)** 63-68.

20. Ortengren U, Andersson F, Elgh U, Terselius B & Karlsson S (2001) Influence of pH and storage time on the sorption and solubility behaviour of three composite resin materials *Journal of Dentistry* **29(1)** 35-41.
21. Prakki A, Cilli R, Mondelli RF, Kalachandra S & Pereira JC (2005) Influence of pH environment on polymer based dental material properties *Journal of Dentistry* **33(2)** 91-98.
22. Pearson GJ & Longman CM (1989) Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system *Journal of Oral Rehabilitation* **16(1)** 57-61.
23. Beatty MW, Swartz ML, Moore BK, Phillips RW & Roberts TA (1993) Effect of crosslinking agent content, monomer functionality, and repeat unit chemistry on properties of unfilled resins *Journal of Biomedical Materials Research* **27(3)** 403-413.
24. Tay FR, Pashley DH, Yiu C, Cheong C, Hashimoto M, Itou K, Yoshiyama M & King NM (2004) Nanoleakage types and potential implications: Evidence from unfilled and filled adhesives with the same resin composition *American Journal of Dentistry* **17(3)** 182-190.
25. Marcovich NE, Reboredo MM & Aranguren MI (1999) Moisture diffusion in polyester-woodflour composite *Polymer* **40** 7313-7320.
26. Geurtsen W (1998) Substances released from dental resin composites and glass ionomer cements *European Journal of Oral Sciences* **106(2)** 687-695.
27. Ortengren U (2000) On composite resin materials. Degradation, erosion and possible adverse effects in dentists *Swedish Dental Journal* **(Supplement 141)** 1-61.
28. Hasegawa T, Manabe A, Itoh K & Wakumoto S (1989) Investigation of self-etching dentin primers *Dental Materials* **5(6)** 408-410.
29. Hotta M, Kondoh K & Kamemizu H (1998) Effect of primers on bonding agent polymerization *Journal of Oral Rehabilitation* **25(10)** 792-799.
30. Tay FR, Moulding KM & Pashley DH (1999) Distribution of nanofillers from a simplified-step adhesive in acid-conditioned dentin *Journal of Adhesive Dentistry* **1(2)** 103-117.
31. Ortengren U, Wellendorf H, Karlsson S & Ruyter IE (2001) Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment *Journal of Oral Rehabilitation* **28(12)** 1106-1115.
32. Santerre JP, Shajii L & Leung BW (2001) Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin-derived products *Critical Reviews in Oral Biology and Medicine* **12(2)** 136-151.
33. Shastri VP, Hildgen P & Langer R (2003) *In situ* pore formation in a polymer matrix by differential polymer degradation *Biomaterials* **24(18)** 3133-3137.
34. Yiu CK, King NM, Pashley DH, Suh BI, Carvalho RM, Carrilho MR & Tay FR (2004) Effect of resin hydrophilicity and water storage on resin strength *Biomaterials* **25(26)** 5789-5796.
35. Costa CA, Giro EM, do Nascimento AB, Teixeira HM & Hebling J (2003) Short-term evaluation of the pulpo-dentin complex response to a resin-modified glass-ionomer cement and a bonding agent applied in deep cavities *Dental Materials* **19(8)** 739-746.
36. Carrilho MR, Carvalho RM, Tay FR & Pashley DH (2004) Effects of storage media on mechanical properties of adhesive systems *American Journal of Dentistry* **17(2)** 104-108.
37. Frankenberger R & Tay FR (2005) Self-etch vs etch-and-rinse adhesives: Effect of thermo-mechanical fatigue loading on marginal quality of bonded resin composite restorations *Dental Materials* **21(5)** 397-412.