JULIANA MALACARNE ZANON

EFEITO DA PRESENÇA, DO TIPO E DA CONCENTRAÇÃO DE SOLVENTE ORGÂNICO NA PERMEABILIDADE DE SISTEMAS ADESIVOS

Tese apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, para obtenção do Título de Doutor em Materiais Dentários.

Orientador: Profª. Drª. Marcela Rocha de Oliveira Carrilho

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Dedico este trabalho,

Às minhas filhas, LARA E VITÓRIA,
para que lhes sirva de exemplo de que as
grandes conquistas são resultado de muita
dedicação e amor.

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"Quando iniciar sua jornada de volta à Ithaca,
peça para que o caminho seja longo, cheio de
aventuras, cheio de acontecimentos;
que sejam muitas as manhãs, quando, com tamanho
prazer, você entrará por portas nunca antes vistas.
Sempre tenha Ithaca em mente.
Chegar lá é seu objetivo!
Mas não se apresse durante a viagem.
É melhor que ela dure por muitos anos
e que você ancore quando estiver rico com tudo o
que aprendeu no caminho.
Não espere que Ithaca te ofereça riquezas.
Ela já te presenteou com essa bela viagem!
Com todo o conhecimento que adquiriu no caminho,
você já deverá ter compreendido o que Ithaca
representa."

Constantine P. Cavafy
(Modificado do poema Ithaca – 1911)

RESUMO

Este estudo, composto por três trabalhos, avaliou o efeito de diferentes tipos e concentrações de solventes orgânicos no grau de conversão (DC) e na permeabilidade de diferentes sistemas adesivos. No primeiro estudo, o DC de cinco adesivos experimentais de composição hidrófila/hidrófoba conhecida (R1<R2<R3<R4<R5), contendo 5%p/p ou 15%p/p etanol, assim como a sorção (WS), a solubilidade (SL) e a cinética de difusão da água (D) nos polímeros obtidos foram mensurados. No segundo estudo, a WS, a SL e a nanoinfiltração de prata (NN) em adesivos experimentais (R2, R3 e R5), polimerizados na presença de 15%p/p etanol ou 15%p/p acetona, foram avaliados após 7 dias (7d) e 6 meses (6m) de armazenamento. No terceiro estudo, foi avaliada a NN em sete adesivos comerciais, formulados com diferentes tipos e concentrações de solventes, para serem aplicados ao substrato dental com diferente número de passos clínicos. Todos os espécimes foram confeccionados em matriz metálica (0,8mm x 5,8mm), aplicando-se 80s de fotoativação a 650mW/cm^2. O DC foi determinado por espectroscopia de infra-vermelho. Para o cálculo de WS, SL e D, os espécimes foram tratados de acordo com as normas da ISO 4049, exceto para os tempos de aferição das massas úmidas, que foram obtidos sequencialmente durante os 7 primeiros dias de armazenagem em água e após 6 meses. Para avaliação da nanoinfiltração, os espécimes foram infiltrados com nitrato de prata amoniacal, conforme protocolo de nanoinfiltração (Tay et al., 2002), exceto pelo tempo que os espécimes permaneceram na solução de nitrato de prata (48 h). Em seguida, os mesmos foram preparados para observação em microscópio eletrônico de varredura. Os valores obtidos de DC, WS, SL e D foram submetidos à análise de variância e, em seguida, ao teste de Tukey (α=0,05). A presença de etanol aumentou o DC de todas as resinas avaliadas, especialmente as mais hidrófobas R1 e R2 ($p<0,05$). A WS, a SL e o D dos adesivos experimentais aumentaram com a hidrofilia. Em geral, as resinas contendo 15% de solvente exibiram maior WS, SL e D que suas correspondentes não-solvatadas ou contendo 5% de solvente ($p<0,05$). Não foram encontradas diferenças significativas entre os tipos de solventes presente ($p>0,05$). Diferenças significativas entre os tempos de avaliação de WS, de SL e de NN, em geral, foram encontradas para os espécimes mais hidrófilos ($p<0,05$).

Os componentes menos hidrófilos dos sistemas adesivos indicados para serem aplicados utilizando-se maior número de etapas clínicas mostraram menor NN que os sistemas adesivos “simplificados”. Adesivos hidrófilos apresentaram diferentes permeabilidades em solução aquosa. Os mais hidrófilos, contendo maiores concentrações de solventes orgânicos, são mais permeáveis e, consequentemente, mais susceptíveis à degradação ao longo do tempo.

Palavras-chave: adesivos dentais, durabilidade, sorção, solubilidade, nanoinfiltração, permeabilidade.

ABSTRACT

This study evaluated the effect of different solvent types and concentrations on the degree of conversion (DC) and permeability of different adhesive systems. In the first study, the DC of five experimental adhesives of known hydrophilicity based on their solubility parameters (R1<R2<R3<R4<R5), added with 5 wt% or 15 wt% ethanol, were evaluated. Additionally, water sorption (WS), solubility (SL) and diffusion coefficient of water (D) through the polymerized materials were also assessed. In the second work, the WS, SL and nanoleakage (NN) in model adhesives (R2, R3 e R5), polymerized in the presence of 15 wt% ethanol or 15 wt% acetone, were evaluated after 7 days (7d) and 6 months (6m) of water storage. In the third work, it was assessed the NN in seven commercial adhesive systems, formulated with different solvent types and concentrations, to be applied on dentin under different clinical approaches. All specimens were produced on teflon molds (0.8mm X 5.8mm), with 80 s of photoactivation, under 650 mmW/cm^2. The DC was determined by infra-red spectroscopy. For WS, SL and D evaluations, specimens were treated according to ISO 4049, except for the times of m_2 measurements, which were collected successively during the first 7 days of storage in water, and, then, after 6 months. For NN, specimens were stored in silver nitrate solution, according to the protocol reported by Tay et al. (2002), and then prepared for scanning electron microscopy evaluation. Values of DC, WS, SL and D were analyzed by ANOVA and Tukey's test (α=0,05). Ethanol addition increased the DC of all tested resins, but specially of the most hydrophobic ones, R1 and R2 ($p<0.05$). Permeability increased with the hydrophilicity of resin blends. In general, solvated resins exhibited significantly higher permeability than their correspondent neat versions ($p<0.05$). The only exceptions were R1 and R5, the least and the most hydrophilic adhesives respectively. Both exhibited similar WS values for neat and solvated versions ($p>0.05$). There were no significant differences when compared both solvents ($p>0.05$). Differences in WS, SL and NN, attributable to different times of water storage, were found for neat and solvated versions of R5. NN in the less hydrophilic components of commercial adhesive systems, indicated to be applied on dentin under multiple steps, were less evident than that observed in "simplified" adhesives. Based on the limitation of this study, it was concluded that more hydrophilic and solvated adhesives are more permeable to fluids diffusion and more vulnerable to water degradation effects over time.

<u>Key Words</u>: adhesives, durability, sorption, solubility, nanoleakage, permeability.

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INTRODUÇÃO

A partir da década de 80, a técnica de hibridização dos tecidos duros, empregando sistemas adesivos, estabeleceu-se como método eficaz de retenção do material restaurador à estrutura dental (Nakabayashi, Kojima & Matsuhara, 1982), viabilizando a execução de procedimentos mais conservadores que aqueles permitidos pelos recursos vigentes até o momento (Nakabayashi & Pashley, 1998).

Os sistemas adesivos atuais se constituem de uma mistura de monômeros resinosos hidrófilos e hidrófobos, geralmente dissolvidos em solventes voláteis, como acetona e etanol, podendo ainda conter água. Enquanto os monômeros resinosos são responsáveis pela formação da camada híbrida e copolimerização com o compósito restaurador, os solventes respondem pela fluidez da solução e pelo deslocamento da água presente na superfície dentinária desmineralizada, facilitando, dessa forma, a infiltração da mistura monomérica nos espaços microscópicos criados na estrutura dental, após seu condicionamento (Carvalho et al., 2004).

São inegáveis os altos valores imediatos de resistência de união alcançados com o emprego destas formulações. No entanto, avaliações longitudinais das restaurações adesivas têm identificado quedas acentuadas dos valores de resistência reportados, após curtos períodos de tempo (De Munck et al., 2003; Carrilho et al., 2004; Hashimoto et al., 2007; Torkabadi et al., 2008), justificando falhas clínicas, como a recorrência de cárie, a sensibilidade pós-operatória e a descoloração de margens, observadas em avaliações de longo prazo (Mjör, 1997; Mjör & Moorhead, 2000; Peumans et al., 2007).

A queda nos valores de resistência mecânica da interface de união, após seu envelhecimento em água, tem sido atribuída não somente à degradação das estruturas proteicas que a compõem, quais sejam as fibrilas de colágeno (Hashimoto et al., 2002, 2003), mas principalmente à instabilidade da resina adesiva quando submetida às condições que simulam o meio bucal (Burrow et al., 1996; Tay et al., 2003a; Carrilho et al., 2005). Recentemente, foi demonstrada uma relação direta entre o caráter hidrófilo das resinas adesivas e a queda de suas propriedades mecânicas ao longo do tempo (Yiu et al., 2004), sendo a afinidade química destas moléculas com a água apontada como a causa principal para tal comportamento.

O efeito da água na estrutura dos materiais é usualmente estudado em função de seu reconhecido potencial degradante (Santerre, 2001). A água pode participar ativamente na clivagem das ligações poliméricas, como também servir de meio para a ação de enzimas. No caso dos sistemas adesivos, que são constituídos predominantemente por monômeros derivados da esterificação do ácido metacrílico, este efeito se torna ainda mais marcante, devido à suscetibilidade das ligações do tipo éster à clivagem por hidrólise (Göpferich, 1996). Assim, qualquer característica da resina adesiva que favoreça maior interação da mesma com a água parece contribuir, em última análise, para acelerar a degradação do componente resinoso das interfaces de união.

Com base nisso, a técnica adesiva deveria envolver, idealmente, a aplicação de adesivos dentais, constituídos exclusivamente por monômeros hidrófobos de alto peso molecular, em substrato seco (Carvalho et al., 2004). Ao contrário, os sistemas adesivos têm sido constituídos por substâncias cada vez mais hidrófilas adicionadas de solventes orgânicos, devido à necessidade de serem aplicados em meio úmido. A permanência de tais solventes na mistura monomérica, previamente a sua fotoativação, tem sido apontada como determinante para a formação de áreas de incompleta conversão monomérica (Paul et al. 1999; Miyasaki et al., 2003), responsáveis por uma camada adesiva porosa e, conseqüentemente, ainda mais permeável ao trânsito de fluidos (Tay et al., 2003b e 2004; Itthagarun et al., 2004; Chersoni et al., 2004). Ante a tal condição, a completa evaporação da mistura solvente/água presente na formulação dos adesivos passou a ser extensamente recomendada. Contudo, dois fenômenos parecem se contrapor à obtenção desse requisito: maior interação química entre monômeros e solventes à medida que mais monômeros hidrófilos são adicionados à mistura (Yiu et al., 2006); e redução da pressão de vapor dos solventes, causada pelo aumento da concentração de monômeros na mistura à medida que parte desse solvente se volatiliza (Pashley et al., 1998; Perdigão et al., 2001; Carvalho et al., 2003). Assim, apesar de requerida, a completa evaporação de solventes e água de formulações adesivas tem se mostrado difícil ou impossível de ser obtida (Yiu et al., 2005; Ikeda et al., 2005; Nunes et al, 2006)

Considerando que solvente residual pode permanecer nos adesivos antes de sua polimerização, este estudo teve por objetivo geral avaliar o efeito do tipo e da concentração de solventes orgânicos no grau de conversão e na permeabilidade (sorção/solubilidade/nanoinfiltração) de sistemas adesivos conhecidamente hidrófilos, afim de elucidar a contribuição dos mesmos nos processos de deterioração do componente adesivo polimérico das interfaces de união.

CAPÍTULO 1

Effects of ethanol addition on the water sorption/solubility and percent conversion of comonomers in model dental adhesives

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Short title: *water diffusion/percent conversion of ethanol-solvated adhesives*

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Abstract

Objectives: This study evaluated the kinetics of water uptake and percent conversion in neat *versus* ethanol-solvated resins that were formulated to be used as dental bonding agents. *Methods:* Five methacrylate-based resins of known and increasing hydrophilicities (R1, R2, R3, R4 and R5) were used as reference materials. Resins were evaluated as neat bonding agents (100% resin) or they were solvated with absolute ethanol (95% resin/5% ethanol or 85% resin/15% ethanol). Specimens were prepared by dispensing the uncured resin into a circular mold (5.8 mm x 0.8 mm). Photo-activation was performed for 80 s. The water sorption/diffusion/solubility were gravimetrically evaluated, while the degree of conversion (DC) was calculated by Fourier-transform infrared spectroscopy. *Results:* Water sorption increased with the hydrophilicity of the resin blends. In general, the solvated resins exhibited significantly higher water sorption, solubility and water diffusion coefficients when compared to their corresponding neat versions ($p<0.05$). The only exception was resin R1, the least hydrophilic resin, in which neat and solvated versions exhibited similar water sorptions ($p>0.05$). Addition of ethanol increased the DC of all tested resins, especially of the least hydrophilic, R1 and R2 ($p<0.05$). Despite the increased DC of ethanol–solvated methacrylate-based resins, it occurs at the expense of an increasing in their water sorption/diffusion and solubility values. *Significance*: Negative effects of residual ethanol on water sorption/solubility appeared to be greater as the hydrophilicity of the resin blends increased. That is, the use of less hydrophilic resins in dental adhesives may create more reliable and durable bonds to dentin.

Keywords: dental adhesives, residual ethanol, water sorption/solubility, percent conversion.

Introduction

In contemporary dental adhesives, high concentrations of relatively hydrophilic methacrylate monomers (i.e. HEMA, BPDM, PENTA) are generally blended with relatively hydrophobic adhesive monomers (i.e. Bis-GMA, UDMA) to enhance bonding to intrinsically water-wet dentin. To facilitate the mixing of hydrophilic with hydrophobic monomers and to avoid phase separation between these components, manufactures have also added volatile solvents such as ethanol and acetone when formulating dental adhesives [1]. The presence of hydrophilic monomers and volatile solvents improves the wetting performance of dental adhesives when applied to acid-etched dentin that is intentionally saturated with water. Volatile solvents facilitate the displacement of water from the acid-etched dentin matrix [2], ensuring better monomers penetration into the micro- and nanoporosities left between the collagen fibrils [3] and, thus, improving their micro-retention to the tooth substrate [4,5].

Conversely, the presence of residual solvent/water before the photo-activation of adhesives and formation of hybrid layers has been thought to be responsible for producing localized areas of incomplete monomer polymerization [6-8], generating porosities within bonded interfaces that, in turn, may permit inward diffusion of oral fluids [9-13]. Recent reports have shown, however, that water uptake is dependent not only on the presence of residual solvent but is also determined by the degree of hydrophilicity of the materials [14-16]. The high concentration of hydrophilic comonomers in dental adhesives alters the colligative properties of the entire mixture, lowering the vapor pressure of volatile components, such as nonpolymerizable solvents (i.e. acetone, ethanol, water) [17]. It is reasonable to consider, therefore, that the presence of residual solvent, combined with the use of hydrophilic comonomers applied to wet dentin may synergistically compromise the requirements for perfect sealing and durable coupling between resin composites and resin-bonded dentin

Although the influence of residual volatile solvent on the kinetics of water sorption/solubility in dental adhesives has been theoretically considered [11,12,15, 18,19] or, even indirectly studied [20], to the best of our knowledge there are no studies where the relationship among these variables (i.e. presence of solvent, degree of resin hydrophilicity and water sorption/solubility behavior) has been investigated together. This lack of information is probably related to the fact that is quite impractical to investigate commercial adhesives of unknown quantitative composition. Thus, the purpose of this study was to analyze whether the addition of 5 or 15% ethanol to experimental dental adhesives of known composition and hydrophilicity could affect their water sorption and percent conversion. The amount of added ethanol simulated the clinical condition where complete elimination of the solvent was not reached [21]. Thus, the tested hypotheses were that addition of 5 or 15% ethanol to experimental, methacrylate-based adhesives of increasing hydrophilicity can: 1) increase their water sorption, solubility and water diffusion coefficients and 2) decrease their degree of conversion.

Material and Methods

Five experimental comonomer resin blends (R1, R2, R3, R4 and R5) were evaluated as potential dentin/enamel adhesive systems. These experimental resin blends were purposely formulated to be ranked in an increasing order of hydrophilicity (R1<R2<R3<R4<R5), based on their Hoy's solubility parameters for hydrogen bonding or total cohesive energy [12,22], as listed in Table 1. Resins R4 and R5 contain comonomers with acidic functional groups that are methacrylate derivatives of carboxylic or phosphoric acids, respectively. They are similar to one-step self-etch adhesives [14,22] and very hydrophilic when compared to resins R1 and R2, which consist of relatively more hydrophobic dimethacrylates. Resins R1 and R2, therefore, are similar to non-solvated bonding agents of three-step etch-and-rinse and two-step self-etch adhesive systems [22]. Resin R3 has an intermediary hydrophilicity and contains a typical composition of two-step etch-and-rinse adhesives [22]. These experimental resins were used in the form of either neat or solvated resins that were mixed with absolute ethanol to produce primers, containing 95% comonomers/5% ethanol or 85% comonomers/15% ethanol (w/w %). Freshly prepared mixtures were ultra-sonicated for 5 minutes in closed containers to ensure homogeneity.

Resin disk preparation

Twenty resin disks (n=20) of each experimental comonomer resin blend (neat and solvated) were produced in a brass mold (5.8 mm diameter, 0.8 mm thick). The liquid comonomers (approximately 50 μL) were directly dispensed to completely fill the mold. Solvent evaporation was not performed as the aim of the study was to evaluate the effect of known ethanol concentrations on the kinetics of water diffusion and percent conversion of such experimental resins. A glass cover slip was then placed on the top of the resins to exclude atmospheric oxygen, ethanol evaporation and displace excess solution. Photo-activation was immediately performed using a quartz-tungsten-halogen-light source at delivered 650 mW/cm^2 for 40 s (Elipar TriLight, ESPE, Germany). After removal from the mold, the bottom of the resin disks was further photo-cured for another 40 s. Selection of curing time was determined in a pilot experiment by measuring a baseline microhardness of the surface of the resin disks (unpublished data). With the adopted total curing time (80 s) resins exhibited a mean Knoop microhardness of 20 ± 2 KHN that was sufficient to allow specimens to be removed from the brass mold without undergoing permanent deformation. The twenty specimens produced with each experimental neat and solvated resin were randomly divided into 4 groups of five specimens (n=5 per group) to evaluate the diffusion coefficient of water, the water sorption and solubility in two different periods (after 7 days and 6 months of storage in water) and the degree of conversion.

Diffusion coefficient of water

After preparation, the resin disks were all pre-dried in a sealed desiccator containing fresh silica gel (at 37 ºC) and repeatedly weighed at 24-h intervals, until a constant mass (m_1) was obtained (i.e. variation lower than 0.02 mg in 24 h). They were individually immersed in deionized water at 37 ºC for measurement of the diffusion coefficient of water in the resins. At fixed time intervals, the specimens were removed from the vials, washed in running water for 5 s, blot-dried, weighed and returned to water. Several readings were taken during the first day (every 30 minutes for 12 hours), and then at increasing intervals (every 12 hours) until equilibrium of specimen mass was attained. The diffusion coefficients of water in the experimental resins were determined by plotting the M_t/M_∞ ratios as a function of the square root of time (where M_t was the mass gain after time t and M_∞ was the final mass gain). Since all plotted curves were linear when $M_t/M_\infty \leq 0.5$ (not shown), the diffusion coefficients of water (D) in the resins could be calculated using the Stefan's approximation [23]:

$$\frac{M_t}{M_\infty} = \frac{4}{L}.\left(\frac{Dt}{\pi}\right)^{1/2} \tag{1}$$

where *L* is the thickness of the specimen (in cm).

The calculation of the diffusion coefficient of water was based only on the increases in wet mass due to water sorption, that is, loss of specimen mass by release of resin compounds/water was not included. The diffusion coefficients of water in neat and solvated resins were analyzed by two-way ANOVA, with the type of resin blend and the amount of solvent present in the mixture as the main factors. Post-hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at α=0.05.

Water sorption and solubility evaluation

Water sorption and solubility were determined using the following modifications to ISO 4049, which includes smaller specimen dimensions (5.8 mm in diameter, instead of 15 mm) and longer periods of water gain/loss measurements (i.e. besides the analysis after the seventh day of storage in water, they were also tested after 6 months of storage in water). After a constant dry mass (m_1) was obtained (as described previously), the resin disks were individually immersed in deionized water at 37 ºC for water sorption and solubility evaluation. After time intervals of 7 days and 6 months, the resin disks were washed in running water, gently wiped with absorbent paper, and weighed in an analytical balance for m_2 determination. The disks were then re-dried in a desiccator, as previously described, and weighed daily up to a dried constant mass (m_3) was obtained. Water sorption (WS) and solubility (SL) were calculated after 7 days (7 d) or 6 months (6 m) of water immersion using the following formulae [24]:

$$WS = \frac{m_2 - m_3}{V} \qquad SL = \frac{m_1 - m_3}{V} \tag{2}$$

where V is the volume of each resin disk (in mm^3).

Means of water sorption and solubility were analyzed by two individual three-way ANOVA (one for water sorption and other for solubility data), having as main factors: the type of resin blend (R1, R2, R3, R4 or R5), the amount of solvent present in the mixture (none, 5% or 15% ethanol) and the storage time (7 d or 6 m). Post-hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at α=0.05.

Degree of resins conversion

Following curing and storage in a desiccator for obtaining a constant dry mass, the resin disks were pulverized into fine powder using an agate mortar and pestle. Resin powder was mixed with infrared grade potassium bromide (KBr) powder at a ratio of 3:180 mg [25]. Five KBr pellets were obtained from each of tested cured resins. Infrared-spectra of KBr/resin pellets were collected in transmission mode using a Fourier transform infrared spectroscopy (FTIR Shimadzu 8300, Shimadzu, Tokyo, Japan) equipped with a KBr beam splitter and a mercury cadmium telluride detector. A blank KBr pellet was used for the collection of the background spectrum. For each specimen, multiple spectra were collected in the range of 4000 ~ 650 cm^{-1} at a resolution of 4 cm^{-1}. FTIR-spectra of uncured resins were also obtained as reference for calculation of the degree of conversion (DC). From the absorbance of uncured resins, a calibration curve was generated allowing for correlation of (C=C) absorption ratios with known molar concentration ratios. The degree of conversion was calculated from the equivalent aliphatic (absorbance peak located at 1638 cm^{-1})/aromatic (absorbance peak located at 1608 cm^{-1}) molar ratios of cured (C) and uncured (U) specimens [26]. Percentage of degree of conversion (%DC) of all neat and solvated resin blends was estimated based on the formula:

$$\%DC = \left(\frac{1-C}{U}\right) \times 100 \qquad (3)$$

Degree of conversion for neat and solvated resins was analyzed by a two-way ANOVA with the amount of solvent present in the mixture and the resin type as the two factors. Post-hoc multiple comparisons were performed using Tukey’s test. Statistical significance was preset at $\alpha=0.05$.

Results

Diffusion coefficient of water

Results of measurements of the diffusion coefficients of water in the neat and solvated resins are summarized in table 2. In general, the neat versions of the experimental resins exhibited diffusion coefficients of water that were significantly lower compared to their correspondent ethanol-solvated version ($p<0.05$). It was not possible to calculate a precise diffusion coefficient of water in resin R1, since it did not present a significant mass gain during the whole period of storage in water. Both solvated versions of resin R5 (5%

and 15% ethanol), the most hydrophilic among the tested mixtures (Table 1), exhibited the greatest water diffusion coefficient ($p<0.05$). Conversely, the lowest water diffusion coefficient was observed for neat resin R2 ($p<0.05$), one of the least hydrophilic resins (Table 1). Water diffusion coefficients for resins R3 and R4 were in the same order of magnitude ($p>0.05$) that, in turn, were significantly higher in comparison to resin R2, considering the neat and 5% ethanol-solvated versions ($p<0.05$); while R3 and R4 had water diffusion coefficients significantly lower when compared to resin R5 ($p<0.05$), regardless their state of solvation (neat or solvated). Differences between the solvated versions of experimental resins (5% and 15% ethanol) were significant only for resin R2, with R2 + 15% ethanol exhibiting a greater diffusion coefficient for water than R2 + 5% ethanol ($p<0.05$).

Water sorption

Results of water sorption of the neat and solvated experimental resins are summarized in Table 3. In general, the neat resins exhibited values of water sorption that were significantly lower when compared to their correspondent ethanol-solvated version ($p<0.05$), except for resin R1 (neat=solvated; $p>0.05$) and for resin R5 when analyzed after 6 months of storage in water (neat=solvated; $p>0.05$). The highest values of water sorption were exhibited by neat and solvated versions of resin R5, for both periods of storage in water (7 days and 6 months). The higher the concentration of ethanol present in resin R5, the higher the water sorption. However, such increase in water sorption due to increasing concentrations of ethanol addition into R5 was only significant at the 7th day of water storage ($p<0.05$). Conversely, the lowest water sorption was shown by neat and solvated versions of resin R1 ($p<0.05$). The presence of ethanol (5 or 15%) and the period of storage in water (7 days or 6 months) did not alter significantly the water sorption behavior of resin R1 ($p>0.05$). For resins R2, R3, R4 and R5, the larger the concentration of ethanol present in the mixture, the greater was the amount of absorbed water. For all these resins, the increase in water sorption due to the increasing in ethanol concentration was significant when specimens were tested at the seventh day of storage in water ($p<0.05$). However, after 6 months of water immersion, the increase in water sorption was significant only for the groups composed by resins R2 and R3 ($p>0.05$) (Table 3). Mass variation curves during 7 days of immersion in water are shown in Figure 1a-e. Changes in mass were plotted against the storage time in order to obtain the kinetics of water absorption during the first week of water storage. Then, the initial mass determined after the first desiccation process (m_1) was used to calculate the change in mass after each fixed time interval during the first 7 days (i.e. 168 hours) of storage in water. All materials showed the greatest increase of mass within the first 12 or 24 hours of storage in water, except for R1 specimens that did not exhibit a significant mass variation during the whole period of water storage (Figure 1a). A continued increase of mass was observed for neat and ethanol-solvated resins R2, R3 and R4 until the equilibrium was reached, which occurred for all these resins between the first and second day of storage in water (Figure 1b, 1c and 1d). Conversely, after the first 12- or 24 hours of water storage, a constant and significant decrease of mass was seen in neat and solvated resin R5 (Figure 1e).

Solubility

Results of solubility of the neat and ethanol-solvated resins are summarized in Table 4. For most resin blends, the neat resins exhibited solubility values that were significantly lower compared to their corresponding solvated versions ($p<0.05$), except for resin R5, when analyzed after 6 months of storage in water (neat=solvated; $p>0.05$). The highest values of solubility were exhibited by neat and solvated versions of resin R5, regardless of the period of storage in water (7 days and 6 months). The higher the concentration of ethanol present in resin R5, the higher was the solubility value ($p<0.05$). However, differences between the ethanol-solvated versions of resin R5 (5% and 15%) were significant only when the solubility measurement was performed at the seventh day of storage in water ($p<0.05$). Neat resin R1, the least hydrophilic tested material (Table 1), exhibited a solubility value that was significantly higher than neat resins R2, R3 and R4 ($p>0.05$), regardless of the period of storage in water. However, for specimens that were tested at the seventh day of storage in water, the increasing concentration of ethanol (5% *versus* 15%) in R2, R3 and R4 made these resins to exhibit solubility values that were similar (R1+ 5% ethanol = R2+5% ethanol, R3+5% ethanol and R4+5% ethanol, $p>0.05$)

or even superior (R2+15% ethanol, R3+15% ethanol and R4+15% ethanol > R1+15% ethanol, $p<0.05$) to the solubility of ethanol-solvated R1 (Table 4). After 6 months of water storage, it was shown that increasing the concentration of ethanol (5% *versus* 15%) in resin R1 resulted in an increased solubility of the specimens, with the following statistical significance ($p<0.05$) between the solubilities of solvated resins: R1+5% ethanol > R3+5% ethanol and R1+15% ethanol > R2+15% ethanol, R3+15% ethanol and R4+15% ethanol.

Degree of resins conversion

Results of measurements of the degree of conversion of the neat and solvated experimental resins are summarized in table 5. The percent conversion for neat and solvated resins R1-R5 ranged from 43.1 % (neat resin R1) to 71.3 % (5% ethanol-solvated R4). In general, the addition of ethanol into the resin blends increased the conversion of monomers into polymers (Table 5). The highest increase in the percentage of degree of conversion, due to the presence of solvent, was observed for the least hydrophilic resins R1 and R2. For all resins, the degree of conversion of blends solvated with 15% ethanol was significantly higher when compared to their respective neat version ($p<0.05$). Differences in the degree of conversion of resins solvated with 5 *versus* 15% ethanol were significant only for resins R1 and R2 ($p<0.05$). There was no significant correlation between percent conversion and the water sorption/solubility of any of the resins, regardless the period of evaluation (i.e.7 days or 6 months) (data not shown).

Correlations between water sorption/solubility and hydrophilicity of resins

Our previous publications of the water sorption/solubility of neat resins R1-R5 reported highly significant positive correlations between water sorption and Hoy's solubility parameters δ_h, δ_p or δ_t values. The same is true for these relationships in the current paper for water sorption of neat and solvated resins R1-R5 after both 7 days and 6 months. Figure 2 summarizes these data only for 15% ethanol-solvated resins R1-R5 and their total cohesive density parameters δ_t ($p<0.05$). However, similar highly significant results were obtained especially when water sorption of 5% ethanol-solvated resins R1-R5 was plotted against δ_t (after 7 days of water immersion $R^2= 0.95$, $p<0.05$; after 6 months of water immersion $R^2 = 0.93$, $p<0.05$ – data not shown).

There were weak and insignificant correlations between the solubility of neat or solvated resins R1-R5 and their respective Hoy's solubility parameters (data not shown).

Correlations between Hoy's solubility parameters δ_h, δ_p or δ_t values and the other test variables (i.e. diffusion coefficient of water and degree of conversion) were not performed.

Discussion

The results of this study demonstrated that, even in relatively low concentrations (5 or 15%), the addition of ethanol into the tested experimental methacrylate-based dental adhesives increased the ability of these materials to absorb and transport water. The only exception was neat resin R1 which absorbed the lowest amount of water and exhibited a water sorption value that did not differ from those observed for its corresponding ethanol-solvated pairs (R1+5% ethanol; R1+15% ethanol). In general, the extent and rate of water sorption, water diffusion and resin solubility increased with the hydrophilicity of the resin blends. Water uptake profiles showed that, when present, the highest amount of absorbed water occurred at the first 12 hours of the immersion of the test resins in water (Figure 1). Undoubtedly for most of tested conditions, water sorption, solubility and diffusion coefficients were clearly dependent on the hydrophilicity (δ_t) of resins and the presence of residual ethanol. Nevertheless, based on the described exception (data of resin R1), the first tested hypothesis of this study that the addition of ethanol to experimental adhesives of increasing hydrophilicity increases their water sorption, solubility and water diffusion coefficients was only partially supported.

If addition of ethanol had increased the uptake and diffusion of water in all resins, it would have created a linear relationship between the cohesive energy density of the polymer network and their ability to absorb and be permeated by water. In this case, water diffusion could be considered as being more likely dependent on the balance between the macromolecular packing density and the effective free-volume of the formed polymer. However, the low water uptake in the least hydrophilic resins R1 and R2 (neat or solvated), comparatively to the most hydrophilic resins R3 - R5, confirms that resin hydrophilicity is fundamental in determining the rate and extent of water diffusion into these methacrylate-based materials. Thus, we believe that water may have diffused freely through the nanoporosities that were left after evaporation of residual ethanol/unreacted monomers during the desiccation cycle of the specimens, but it may have also diffused as “bound” water, that is, attached to the polar domains present in these experimental resins, as previously described [12,14-16,27].

Since the presence of residual solvent is thought to influence the conversion of monomers into polymer [6,8,21,28-30] by increasing the effective free volume of the formed polymer [15], there was an expectation that ethanol-solvated resins would form specimens that were more prone to absorb water than those formed by non-solvated resins. In fact, such expectation was confirmed. For most resins, the rate and extent of water diffusion in solvated resins was significantly higher than in the neat counterparts (Tables 2 and 3). However, this was not related to the fact that solvated resins were more poorly converted than neat resins (Table 5). Addition of ethanol, indeed, improved the percent conversion of all tested resins, especially of the more hydrophobic resins, R1 and R2. With low concentrations of ethanol (e.g. 15%) the viscosity of the resins may have been reduced to a level where increased intermacromolecular spacing (i.e. increased resin free volume), molecular mobility and growing polymer chain segments might occur [21,28-30]. Such occurrences, in concert, could have been responsible for enhancing the degree of conversion of the model adhesives, which lead us to reject the second tested hypothesis of this study.

The fact that the presence of low concentrations ethanol increased the degree of conversion of the model resins does not mean, however, that one should ignore the requirement of removing as much solvent as possible before dental adhesives polymerization. Increasing the free volume of resins due to the presence of low concentration of ethanol, or any other non-polymerizable polar solvent, may have increased the degree of conversion but it may not be beneficial to the polymer cross-linking. Our results suggest that the concentrations of ethanol used in the present study may have increased the water sorption/diffusion and solubility of solvated model adhesives by interfering with their optimal macromolecular packing density (.i.e. homogeneous macromolecular cross-linking), instead of purely affecting their percent of conversion. In other words, we suggested that while small concentrations of ethanol decreases the viscosity of comonomers blends and allows radical propagation to increase the degree of conversion [20, 28-30]; its presence and non-polymerizable condition also increase the effective free volume of the resin and can prevent the approximation between reactive pendant species, making the cross-linking reaction more difficult [31]. The well-documented correlation between effective removal or complete absence of volatile solvent in dental adhesives and increase in their mechanical properties [7,31,32] is another good reason for not polymerizing these materials in the presence of residual solvent. Polymer networks with homogeneous packing density (i.e. restricted free volume) tend to exhibit at least two desirable properties for a durable function: higher mechanical properties [7,31,33] and lower ability to absorb water [34-36].

Theoretically, solvent and water elimination should be achieved by allowing sufficient evaporation time before polymerization of adhesives. However, complete solvent/water evaporation has shown to be clinically problematic [21,37,38], especially when using the evaporation times recommended by manufacturers [39,40]. In a recent study, for instance, it was shown that experimental adhesives solvated with 50 wt% acetone, 50 wt% ethanol, 50 wt% acetone/water or 50 wt% ethanol/water mixtures retained from 5 to 10% of the added solvent, even after blowing air for 120 s [20], a period 10 times longer than that recommended by the majority of manufacturers of dental adhesives. That study also concluded that the percentage of residual solvent retained in experimental adhesives was significantly influenced by the degree of hydrophilicity of resin monomers, that is, the more hydrophilic was the resin, more solvent it retained [20].

It has been hypothesized that during the first stage of water diffusion, the polymer network is softened by water sorption that causes polymer swelling. Polymer swelling by water reduces the frictional forces between polymer chains [41] (i.e. plasticizes resins). At a high level of absorbed water, polymer chains can undergo a relaxation process, thereby facilitating the elution of unreacted monomers and/or solvents trapped in the polymer network. More hydrophilic polymers, that have a superior capacity of relaxation, may permit faster elution of unreacted monomers/solvents than more hydrophobic polymers [42,43]. This was probably why the most hydrophilic resins R4 and R5 – neat or solvated - showed a high and long-lasting solubility when compared to less hydrophilic resins, such as R2 and R3 (Table 4). Resins R4 and R5 (both neat and solvated) were the only resins that continued to lose mass after 6 months of water immersion (data not shown). At a long-term, the continuous solubility of hydrophilic resin blends may represent a factual hydrolytic breakdown of resin compounds, instead of a simple release of unreacted and/or pendent monomers.

Theoretically, our calculated water diffusion coefficients may have been under-estimated, since they were based on water sorption data alone (i.e. increases in wet mass). Since net increase in wet mass may include loss of dry mass due to simultaneous solubilization of unreacted monomers, the true gain in wet mass may have been greater than was reported. This error would be proportional to the degree of solubilization that, in the current study, varied widely.

Nevertheless, resin hydrophilicity cannot explain, in principle, why the least hydrophilic neat resin R1 exhibited higher solubility than neat resins R2, R3 and R4. In that case, the structural features of the copolymers formed by neat resin R1 may provide a better explanation for their solubility behavior. Apart from the resin hydrophilicity, the relaxation capacity of a polymer network may be also dependent on the degree of conversion and homogeneity of polymer cross-links [34]. It is clear that neat resin R1 exhibited the lowest percent of conversion (43.1% - Table 5) of all five test resins. Neat resin R1 is basically composed of ethoxylated Bis-GMA (Bis-GMA-E) and TEGDMA (Table 1), while the other neat resins are composed by different combinations of Bis-GMA with HEMA, 2MP, TCDM and/or TEGDMA. In high concentration, Bis-GMA-E was reported to give lower degrees of conversion compared to Bis-GMA, UDMA and TEGDMA [44]. In addition, the absence of hydroxyl groups in the backbone of Bis-GMA-E leads it to the formation of polymers that are more flexible than those formed by Bis-GMA [34]. Lower degree of conversion and higher flexibility may explain the high solubility of ethoxylated Bis-GMA-based resins [15,34] (Table 4).

From the profile of the mass variation seen in resins R1-R5 during immersion in water

(Figure 1), it was shown that, in general, more water could enter into solvated resins than into neat resins, at least within the first 12-24 hours of water immersion. Likewise, after obtaining maximum water sorption, the rapid loss of mass observed for solvated resins indicates that they formed less compacted polymer networks that, in turn, imposed lower resistance to the elution of residual ethanol and/or unreacted monomers than did the neat resins. In fact, the presence of solvents (i.e. ethanol, water, acetone), either dispersed among the polymer chains or hydrogen-bonded to polar domains, it is thought to cause additional plasticization by increasing swelling and/or relaxation of polymer network [45,46], which also explains why the experimental ethanol-solvated adhesives showed higher solubility than their neat counterparts (Table 4).

While lower polymer chain cross-linking in these ethanol-solvated methacrylated-based resins seems to offer a theoretical explanation for their higher susceptibility when immersed in water (i.e. water sorption, diffusion and solubility), the effect of the degree of polymers cross-linking on the kinetics of water diffusion should be accurately investigated in future studies.

Under the limited conditions of this study, the present results suggest that there are competing trends operating in resin bonding. Increases of the degree of conversion of adhesives by ethanol addition are not sufficient to form impervious polymerized adhesives. Accordingly, even well-converted adhesives might keep allowing water/moieties diffusion (i.e. solvated resin R4, Table 5), especially if they exhibit a patent hydrophilic nature. The negative effect of residual ethanol on water sorption/diffusion appeared to be even more critical for hydrophilic resin blends. Thus, the amount of solvent incorporated in resins is a critical step in formulating dental adhesives. While solvent should be sufficient to increase the percent conversion of resins, decrease the viscosity of the comonomers and facilitate the displacement of water from dentin, it should not increase the capability of these resins for water sorption/diffusion and solubility. Since hydrophobic resins are less permeable to water and may have their degree of conversion increased by small amounts of ethanol (i.e. 5 – 15%), studies should be performed in order to test whether solvated-hydrophobic monomers could create reliable and durable bonds to dentin.

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Table 1: Composition and Hoy's solubility parameter of the experimental polymers used in the study.

				Hoy's solubility parameters (MPa)$^{1/2}$			
	Resin	Composition	% (w/w)	δ_d	δ_p	δ_h	δ_t
Neat Resin (Polymer)	R1	Bis-GMA-E TEGDMA CQ EDMAB	70.00 28.75 0.25 1.00	15.44	10.59	6.17	19.71
	R2	Bis-GMA TEGDMA CQ EDMAB	70.00 28.75 0.25 1.00	15.58	12.1	8.64	21.54
	R3	Bis-GMA HEMA CQ EDMAB	70.00 28.75 0.25 1.00	15.37	13.02	9.94	22.46
	R4	Bis-GMA TEGDMA TCDM CQ EDMAB	40.00 28.75 30.00 0.25 1.00	16.21	12.61	9.3	22.55
	R5	Bis-GMA HEMA 2MP CQ EDMAB	40.00 28.75 30.00 0.25 1.00	15.76	14.37	10.75	23.88
Solvated resins (Polymer)	R1 + 5%E	R1 Ethanol	95.00 5.00	15.30	10.62	6.86	19.85
	R2 + 5%E	R2 Ethanol	95.00 5.00	15.43	12.05	9.21	21.64
	R3 + 5%E	R3 Ethanol	95.00 5.00	15.23	12.93	10.44	22.54
	R4 + 5%E	R4 Ethanol	95.00 5.00	16.03	12.54	9.84	22.60
	R5 + 5%E	R5 Ethanol	95.00 5.00	15.60	14.21	11.21	23.90
	R1 + 15%E	R1 Ethanol	85.00 15.00	15.02	10.68	8.24	20.19
	R2 + 15%E	R2 Ethanol	85.00 15.00	15.14	11.96	10.34	21.89
	R3 + 15%E	R3 Ethanol	85.00 15.00	14.96	12.74	11.45	22.74
	R4 + 15%E	R4 Ethanol	85.00 15.00	15.67	12.39	10.91	22.76
	R5 + 15%E	R5 Ethanol	85.00 15.00	15.29	13.89	12.14	23.96

Abbreviations: 2MP: Bis[2-(methacryloyloxy)ethyl] phosphate; Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; Bis-GMA-E: ethoxylated bisphenol A diglycidyl ether dimethacrylate; CQ: camphorquinone; EDMAB: ethyl N,N-dimethyl-4-aminobenzoate; HEMA: 2-hydroxyethyl methacrylate; TCDM: di(hydroxyethylmethacrylate) ester of 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl3-cyclohexene-1,2dicarboxylic anhydride; TEGDMA: triethylene-glycol dimethacrylate; δ_d: dispersion forces; δ_p: polar forces; δ_h: hydrogen bonding forces; δ_t: total cohesive energy density

Table 2: Diffusion coefficient (x $10^{-8} cm^2\ s^{-1}$) of water into the different neat and solvated comonomer mixtures.

	Neat	Solvated - 5% ethanol	Solvated – 15% ethanol
R1	**	**	**
R2	4.1 (0.72) ^{c,C}	11.6 (1.53) ^{b,C}	18.6 (2.05) ^{a,B}
R3	7.1 (0.27) ^{b,B}	18.9 (2.66) ^{a,B}	23.6 (0.30) ^{a,B}
R4	6.2 (0.67) ^{b,B}	14.8 (1.54) ^{a,B}	19.2 (1.41) ^{a,B}
R5	21.5 (1.50) ^{b,A}	79.3 (9.40) ^{a,A}	84.7 (14.98) ^{a,A}

Values represent mean (SD), n=5/group. Groups identified by different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences ($p<0.05$).

** Specimens of R1 did not show a significant mass gain over the preset period to evaluate the coefficient of water diffusion, thus it was not possible to calculate a precise water diffusion coefficient for this resin blend.

Table 3: Water sorption (µg/mm^3) of neat and solvated versions of the experimental resins after 7 days and 6 months of water storage.

	7 Days			6 Months		
	Neat	**Solvated - 5% ethanol**	**Solvated - 15% ethanol**	**Neat**	**Solvated – 5% ethanol**	**Solvated – 15% ethanol**
R1	13.7 (0.16) ^{a,D}	12.5 (2.71) ^{a,D}	15.2 (3.93) ^{a,D}	12.9 (2.11) ^{a,D}	12.0 (2.96) ^{a,D}	11.2 (2.24) ^{a,D}
R2	34.1 (4.47) ^{c,C}	59.3 (3.43) ^{b,C}	83.0 (5.44) ^{a,C}	39.1 (3.00) ^{c,C}	55.6 (3.62) ^{b,C}	82.0 (5.35) ^{a,C}
R3	61.8 (4.20) ^{c,B}	77.6 (3.59) ^{b,B}	103.1 (5.71) ^{a,B}	65.2 (2.39) ^{c,B}	69.6 (1.64) ^{b,B}	101.5 (0.82) ^{a,B}
R4	68.6 (2.21) ^{c,B}	88.9 (4.72) ^{b,B}	110.7 (6.14) ^{a,B}	70.4 (2.04) ^{c,B}	73.1 (2.17) ^{c,B}	90.9 (3.37) ^{b,BC}
R5	160.4 (7.65) ^{c,A}	175.9 (7.61) ^{b,A}	191.7 (6.81) ^{a,A}	143.6 (8.84) ^{d,A}	148.1 (6.31) ^{cd,A}	155.7 (5.06) ^{cd,A}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences($p<0.05$).

Table 4: Solubility (µg/mm^3) of neat and solvated versions of the experimental resins after 7 days and 6 months of water storage.

	7 Days			6 Months		
	Neat	**Solvated - 5% ethanol**	**Solvated - 15% ethanol**	**Neat**	**Solvated - 5% ethanol**	**Solvated – 15% ethanol**
R1	13.7 (0.16) ^{d,B}	28.0 (4.31) ^{c,BC}	27.8 (3.94) ^{c,D}	24.0 (1.97) ^{c,B}	46.1 (7.36) ^{b,B}	86.5 (10.88) ^{a,B}
R2	- 3.5 (4.41) ^{c,C}	24.6 (4.30) ^{b,BC}	49.8 (3.12) ^{a,C}	- 1.7 (2.39) ^{c,C}	33.7 (7.61) ^{b,BC}	58.0 (4.08) ^{a,C}
R3	- 3.5 (5.62) ^{c,C}	20.5 (2.49) ^{b,C}	68.4 (6.53) ^{a,B}	- 1.7 (4.01) ^{c,C}	26.0 (4.35) ^{b,C}	53.8 (2.88) ^{a,C}
R4	4.4 (3.12) ^{d,B}	37.0 (4.76) ^{b,B}	59.5 (3.96) ^{a,BC}	12.7 (3.82) ^{c,B}	37.9 (3.85) ^{b,BC}	67.2 (4.48) ^{a,C}
R5	68.1 (9.57) ^{d,A}	117.3 (6.76) ^{c,A}	141.3 (5.06) ^{b,A}	185.1 (5.06) ^{a,A}	188.5 (6.07) ^{a,A}	195.5 (4.18) ^{a,A}

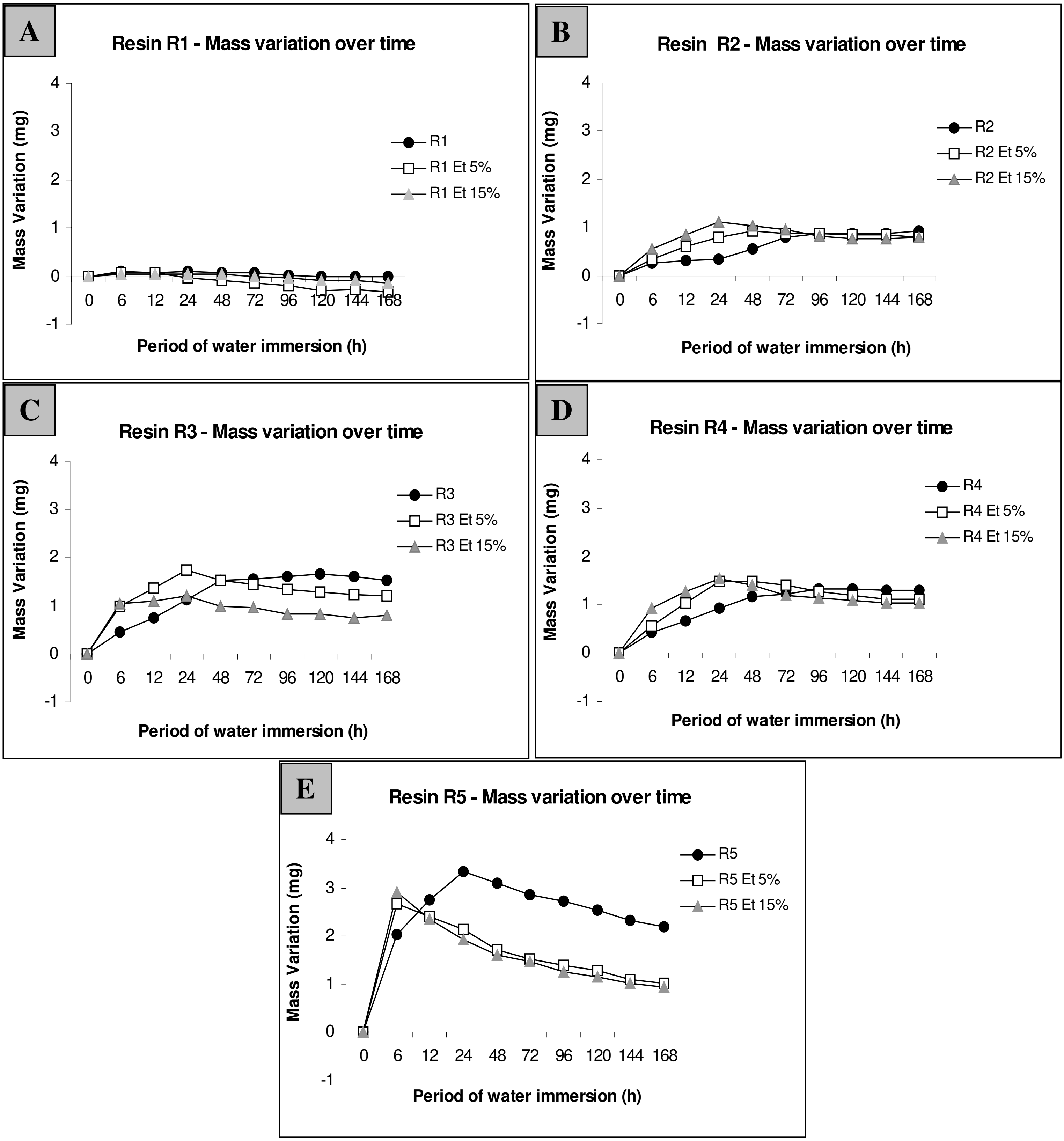
Values represent mean (SD), n=5 (per group). Groups identified with different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences ($p<0.05$). Negative values indicate that after final desiccation the dried constant mass m_3 was higher than m_1, suggesting that the absorbed water may have not been completely eliminated.

Table 5: Degree of conversion (%) of neat and solvated versions of the experimental resins.

	Neat	Solvated – 5% ethanol	Solvated - 15% ethanol
R1	43.1 (2.16) ^{cD}	59.0 (0.93) ^{bC}	63.2 (1.10) ^{aB}
R2	47.2 (0.90) ^{cC}	65.3 (1.45) ^{bB}	69.8 (0.95) ^{aA}
R3	55.1 (1.18) ^{bB}	64.5 (1.05) ^{aB}	63.9 (1.75) ^{aB}
R4	56.5 (2.23) ^{bAB}	71.3 (1.27) ^{aA}	70.5 (1.22) ^{aA}
R5	58.5 (1.06) ^{bA}	62.5 (4.13) ^{abBC}	63.7 (2.24) ^{aB}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences ($p<0.05$).

Figure 1



A
Resin R1 - Mass variation over time
Mass Variation (mg)
4
3
2
1
0
-1
0 6 12 24 48 72 96 120 144 168
Period of water immersion (h)
R1
R1 Et 5%
R1 Et 15%
B
Resin R2 - Mass variation over time
Mass Variation (mg)
4
3
2
1
0
-1
0 6 12 24 48 72 96 120 144 168
Period of water immersion (h)
R2
R2 Et 5%
R2 Et 15%
C
Resin R3 - Mass variation over time
Mass Variation (mg)
4
3
2
1
0
-1
0 6 12 24 48 72 96 120 144 168
Period of water immersion (h)
R3
R3 Et 5%
R3 Et 15%
D
Resin R4 - Mass variation over time
Mass Variation (mg)
4
3
2
1
0
-1
0 6 12 24 48 72 96 120 144 168
Period of water immersion (h)
R4
R4 Et 5%
R4 Et 15%
E
Resin R5 - Mass variation over time
Mass Variation (mg)
4
3
2
1
0
-1
0 6 12 24 48 72 96 120 144 168
Period of water immersion (h)
R5
R5 Et 5%
R5 Et 15%

Figure 1- Mass variation of experimental neat and solvated resins over 7 days of water storage. Symbols represent means values (n=5). Since the standard deviations around all means are smaller than the symbols, they have not been indicated. **A**: Neat and solvated resin R1; **B**: Neat and solvated resin R2; **C**: Neat and solvated resin R3; **D**: Neat and solvated resin R4 and **E**: Neat and solvated resin R5. (Neat resin:—●— ; Resin + 5% ethanol:—□— ; Resin + 15% ethanol: —▲—).

Figure 2

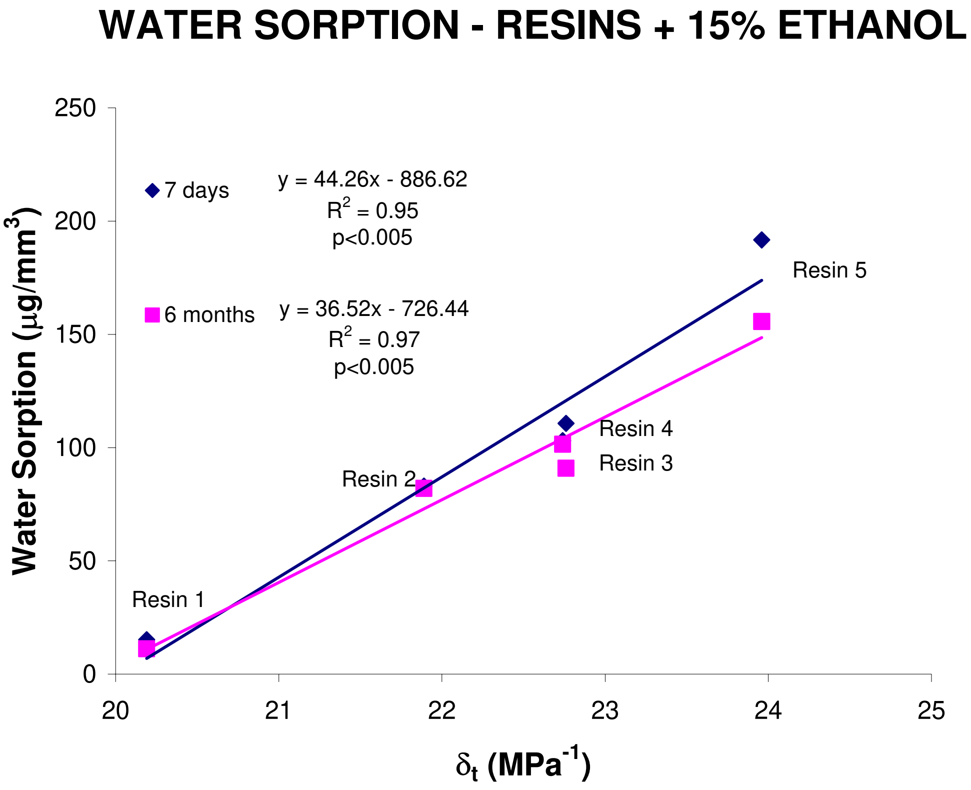


Figure 2- Correlations between the water sorption of 15% ethanol-solvated resins R1-R5 and their respective Hoy's solubility parameter for total cohesive density (δ_t).

CAPÍTULO 2

Effects of solvent type on the water sorption and solubility of model dental adhesives

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ABSTRACT: This study evaluated the effect of solvent type (ethanol or acetone) and time of storage (7 days or 6 months) on the water sorption (WS), solubility (SL) and permeability in three model dental adhesives of known hidrophilicity. Specimens of neat and solvated adhesives were produced and treated according to ISO specification for WS and SL evaluations and to nanoleakage for permeability. In general, solvated adhesives showed higher WS and SL than their non-solvated versions ($p<0.05$), but there were no significant differences when compared both solvents ($p>0.05$). Six-month water storage increased significantly the WS, SL and permeability of the most hydrophilic adhesives ($p<0.05$). Regardless the type of solvent, water diffusion is more pronounced in solvated, more hydrophilic adhesives, stored for prolonged time.

KEYWORDS: dental adhesives, solvents, water sorption/solubility, permeability

INTRODUCTION

To facilitate the mixing of hydrophilic with hydrophobic monomers and to avoid phase separation between these components, manufactures have added volatile solvents when formulating dental adhesives [1]. The presence of hydrophilic monomers and volatile solvents improves the wettability of dental adhesives when applied to acid-etched dentin that is intentionally saturated with water. The most common solvents included into dental adhesives are acetone and ethanol, which are added to the adhesive comonomer mixtures as neat or solvated with water.

Two of the most important properties of solvents are their hydrogen-bond ability and their coefficient of vapor pressure. The hydrogen-bond ability of solvents has been implicated in their capacity to keep the acid-etched dentin matrix in full, partial or diminutive expansion. It has been postulated that the collapse of acid-etched dentin matrices involves the rapid and spontaneous development of new hydrogen bonds between adjacent collagen peptides that results in stiffening of the matrix in a collapsed state [2]. In thesis, as ethanol has higher ability to hydrogen-bonding ($\delta h = 20.0\ (J/cm^3)^{1/2}$) than does acetone ($\delta h = 11.0\ (J/cm^3)^{1/2}$), it can more easily disrupt hydrogen bonding between collagen fibrils, thereby being more indicated for one who intents to keep dentin matrix highly expanded [3] to ensure good adhesive monomers infiltration. Conversely, due to its higher vapor pressure, acetone (200 mmHg at 25 ^{o}C) is thought to be able to displace more water from the dentin matrix than ethanol could do (54 mmHg at 25 ^{o}C), thereby allowing lower drying time and less residual moisture during monomers conversion [4].

If on the one hand the volatile solvents are essential to facilitate the displacement of water from the acid-etched dentin matrix [5], on the other hand their maintenance before the photo-activation of adhesives and formation of hybrid layers has been considered responsible for producing localized areas of incomplete monomer polymerization [6,7], generating porosities within bonded interfaces that may permit inward diffusion of oral fluids [8,9,10] and, then, accelarate the material degradation. Conscious about the drawbacks of not eliminating completely the organic solvent from dentin matrices before adhesives photo-curing, several manufactures have recommended different protocols of air-blowing application to promote further solvent removal. Nevertheless, recent studies have shown that, under the clinical conditions (i.e. short or absent air-blowing time), the complete evaporation of water/solvents from demineralized dentin can be difficult or impossible to achieve [4,11].

Considering that residual amount of solvent can remain trapped into the adhesives before their polymerization, this study aimed to investigate the effect of the type of solvent on the water sorption/solubility and permeability (nanoleakage) of model adhesive blends. It was hypothesized that: 1^{st}) the presence of solvent into model adhesive blends affects its short and long term water sorption and solubility; 2^{nd}) the type of solvent into model adhesives of increasing hydrophilicity has a factual effect on their water sorption/solubility and 3^{rd}) the permeability (nanoleakage) of model adhesives depends on their hydrophilicity and solvent presence.

MATERIAL AND METHODS

Three experimental comonomer resin blends (R2, R3 and R5) were evaluated as potential dentin/enamel adhesive systems. These experimental resin blends were formulated to be ranked in an increasing order of hydrophilicity (R2<R3<R5), based on their triple Hoy's solubility parameters [12,2], as listed in Table 1. Resin R5 contains comonomers with acidic functional groups, which are methacrylate derivatives of phosphoric acids, similar to those found in one-step self-etch adhesives [13,2]. R5 is very hydrophilic when compared to resin R2, which consists of relatively more hydrophobic dimethacrylates. Resin R2, therefore, is similar to non-solvated bonding agents of three-step etch-and-rinse and two-step self-etch adhesive systems [2]. Resin R3 has an intermediary hydrophilicity and contains a typical composition of two-step etch-and-rinse adhesives [2]. These experimental resins were used as neat or solvated resins that were mixed with absolute

ethanol or acetone to produce primers, containing 85% comonomers/15% ethanol or 85% comonomers/15% acetone (w/w %). Freshly prepared mixtures were ultra-sonicated for 5 minutes in closed containers to ensure homogeneity.

Resin disk preparation

Ten resin disks of each experimental comonomer resin blend (neat and solvated) were produced in a brass mold (5.8 mm diameter, 0.8 mm thick). The liquid comonomers (approximately 50 µL) were directly dispensed to completely fill the mold. Solvent evaporation was not performed as the aim of the study was to evaluate the effect of different solvents, and not their amount, on the kinetics of water diffusion in such experimental adhesives. A glass cover slip was then placed on the top of the adhesive to exclude atmospheric oxygen and prevent solvent evaporation. Photo-activation was immediately performed using a quartz-tungsten-halogen-light source at delivered 650 mW/cm^2 for 40 s (Elipar TriLight, ESPE, Germany). After removal from the mold, the bottom of the adhesive disks was further photo-cured for another 40 s. Selection of curing time was determined in a pilot experiment by measuring a baseline microhardness of the surface of the resin disks (unpublished data). With the adopted total curing time (80 s) resins exhibited a minimum Knoop microhardness of 20 ± 3 KNH. The ten specimens produced with each experimental neat and solvated resins were randomly divided into 2 groups of five specimens (n=5 per group) to evaluate the water sorption and solubility in two different periods (after 7 days and 6 months of storage in water).

Water sorption and solubility evaluation

Water sorption and solubility were determined using the following modifications to ISO 4049, which includes smaller specimen dimensions (5.8 mm in diameter, instead of 15 mm) and longer periods of water gain/loss measurements (i.e. besides the analysis after the seventh day of storage in water, they were also tested after 6 months of storage in water [14]). After a constant dry mass (m_1) was obtained, the resin disks were individually immersed in deionized water at 37 ºC for water sorption and solubility evaluation. After time intervals of 7 days and 6 months, the resin disks were washed in running water, gently wiped with absorbent paper, and weighed in an analytical balance for m_2 determination.

The disks were then re-dried in a desiccator and weighed daily up to a dried constant mass (m_3) was obtained. Water sorption (WS) and solubility (SL) were calculated after 7 days (7 d) or 6 months (6 m) of water immersion using the following formulae:

$$WS = \frac{m_2 - m_3}{V} \qquad SL = \frac{m_1 - m_3}{V}$$

where V is the volume of each resin disk (in mm^3).

Statistical analysis

Since the data were normally distributed (Anderson-Darling test), means of water sorption and solubility were analyzed by two individual three-way ANOVA (one for water sorption and other for solubility data), having as main factors: the type of resin blend (R2, R3 or R5), the type of solvent present in the mixture (none, 15% ethanol or 15% acetone) and the storage time (7d or 6m). Post-hoc multiple comparisons were performed using Tukey test. Statistical significance was preset at $\alpha=0.05$.

Permeability evaluation

After the second dessication process, three specimens (n=3) evaluated after each time of water storage (7d and 6m) were randomly selected to be analyzed by means of silver permeation. They were immersed in a 50% ammoniacal silver nitrate solution according to the diamine silver impregnation protocol reported by Tay et al. [15], except that the specimens were maintained immersed in the tracer solution for 48 h, as in a previous study [14] it was seen that the least hydrophilic adhesive (i.e. R2) took up to 48 hours to reach water sorption equilibrium. Afterwards, specimens were rinsed in distilled water, and immersed in a photodeveloping solution for 8 hours, under a fluorescent light, so silver ions could be reduced into metallic silver particles. The silver impregnated specimens were then embedded with epoxy resin and the resultant blocks were cut by the center of the specimens in order to expose the most inner surface. Polishing of the exposed surfaces was obtained using a glass knife attached to an ultra microtome. In this way, washing of the reduced silver granules by humidity contact was avoided. The prepared surface was carbon coated and analyzed by an scanning electron microscope (JEOL-5600 LV, Tokyo, Japan) under backscattered electrons at 90 kV. After this first evaluation, specimens returned more two times to the ultra microtome, for exposing other regions of specimens that were equally prepared to be observed by SEM. Therefore, three different evaluations were performed for each specimen.

RESULTS

Water sorption

Results of WS of neat and solvated experimental adhesives are summarized in Table 2. In general, the neat resins exhibited values of WS that were significantly lower when compared to their correspondent ethanol and acetone solvated versions ($p<0.05$), except for resin R5 when analyzed after 6 months of storage in water (neat=solvated; $p>0.05$). The type of solvent (ethanol or acetone) did not alter significantly the WS behavior of the resins after 7 days of storage nor after 6 months ($p>0.05$). The highest values of WS were exhibited by neat and solvated versions of resin R5, followed R3 and R2 (R5>R3>R2), regardless of the time of storage in water (7 d and 6 m) ($p<0.05$).

Solubility

Results of SL of neat and solvated adhesives are summarized in Table 3. For most resin blends, the neat resins exhibited SL values that were significantly lower compared to their corresponding solvated versions ($p<0.05$), except for resin R5, when analyzed after 6 months of storage in water (neat=solvated; $p>0.05$). The type of solvent (ethanol or acetone) did not alter significantly the SL values of the resins after 7 days of storage nor after 6 months ($p>0.05$). Prolonged time of water immersion (7 d X 6 m) also did not determine significant differences in SL of the neat and the solvated versions of resins, except for R5 and acetone-solvated version of R2, which showed increased values after 6 months ($p<0.05$). The highest values of SL were exhibited by neat and solvated versions of resin R5 ($p<0.05$), regardless of the period of storage in water.

Nanoleakage evaluation

Figures 1 to 3 depict the most characteristics patterns of silver permeation observed along the inner exposed surfaces of the different adhesives, evaluated as neat or solvated resins, after 7 days and 6 months of water storage. In general, silver deposition increased with resin hydrophilicity, being more severe in R5 specimens. After 6 months of water storage, silver deposition increased for R3 and R5, evaluated as neat or solvated. Solvation contributed to increase silver deposits of R5 versions.

DISCUSSION

The results of this study demonstrated that the presence of solvents into the tested experimental dental adhesives increased the ability of these materials to absorb and release moieties during water storage. The only exception was observed to neat adhesive R5, which exhibited water sorption and solubility values that did not differ from its solvated-counterparts, when evaluated after 6 months of storage in water (neat=15% ethanol= 15% acetone). Based on this exception, the first anticipated hypothesis that the presence of solvents into model adhesives blends affects their WS and SL was only partially supported. It was found that the type of solvent added to the comonomer mixture (ethanol or acetone) had no significant effect on the WS and SL of the solvated adhesives, which support the rejection of the second anticipated hypothesis that the type of solvent has a factual effect on the WS and SL of the methacrylate-based adhesives. The higher the hydrophilicity of the adhesive, the higher the silver permeation/deposition observed. On the other hand, solvation of adhesives only affected the short and long-term permeability of the adhesive R5, the most hydrophilic material in this study. Thus, the third anticipated hypothesis that the permeability of model adhesives depends on their hydrophilicity and solvent addition was only partially validated.

Although several WS and SL studies on composites and other hydrophobic/hydrophilic resins has been conducted over many years, WS and SL of polymerized dental adhesives has gained more attention just after these phenomena was shown to be strictly related with the short durability of resin-bonded interfaces [16,17]. Studies have shown that similarly to that observed for methacrylate-based composites [18,19,20,21], the water diffusion in dental adhesives is also dependent on their hydrophilicity (polarity) and network topology [13,14,22]. Thus, water can diffuse freely through polymers nanoporosities as "unbound" water, or tightly attached to polar domains *via* hydrogen bonding.

The increase in the free volume of adhesives due to the presence of solvent may justify the increase in WS and SL of solvated-versions when compared to their neat counterparts. It is suggested that the solvent concentrations used in the present study could have interfered with the optimal macromolecular packing density of the polymerized adhesives (i.e. homogeneous macromolecular cross-linking), by preventing the approximation between reactive pendant species [23] and leading to the formation of loosely packed polymer network. Taking into account that the presence of solvent during adhesive's polymerization determined an increase in WS and SL of adhesives and that the highest WS and SL was observed for the most hydrophilic material (R5), one could assume that indeed the two deleterious factors evaluated in this study – adhesive's hydrophilicity and solvation equally interfere with adhesive permeability. Nevertheless, since the neat and solvated versions of the most hydrophilic adhesive (R5) exhibited similar values of WS and SL after 6 months of storage in water (Table 2-3), it is possible to consider that at long-term the water diffusion and resin moieties elution is likely more dictated by the hydrophilicity of adhesives and, then, the ability of water to diffuse while attached to the adhesive polar domains.

The amount of silver deposits among R2, R3 and R5 specimens were clearly different (Fig. 1-3). Such differences, however, was not evident between the neat *versus* the solvated versions of the same hydrophobic resin (R2 or R3), differing from the results obtained for WS and SL. In virtue of that, it is prudent to consider that the permeability to water and silver ions may occur differently. While water is able to diffuse through the polymer by successively binding hydrogen bonds even in the absence of nanovoids, silver ions may need additional opening of free space to accommodate. According to the interaction theory [24,25], “bound” water diffusion is able to disrupt interchain hydrogen bonds, inducing swelling and thus additional opening of free volume, as the polymer is kept in water. Such additional opening seems imperative to allow significant amount of silver diffusion trough more hydrophobic materials. The total amount of free volume capable to be attained with swelling is relative to the hydrophilicity and cross-linking density of the polymer network [26,18,19]. Thus, the more hydrophilic and loosely cross-linked the polymer, the higher the relaxation between polymer’s chains under storage in water. Accordingly, it can be suggested that relaxation have highly taken place within the most hydrophilic adhesive (R5) right after its storage in water so that it could allow higher uptake of silver particles, making the visualization of silver granules possible even at the short-term (Fig 3). For R3 ,the adhesive with intermediate hydrophilicity, the visualization of silver granules was only possible after prolonged time of water storage (i.e., 6 months), while for R2, the least hydrophilic adhesive, even 6-month water storage was not sufficient to allow visual observation of silver granules deposition.

Although the hydrophilicity of adhesives may play a preponderant role in their WS and SL behavior, it is not possible to ignore that the presence of solvent had an extra effect on the permeability of these adhesives. An intense silver deposition, combined with severe margin distortion and crack formation, were observed in all R5 solvated specimens (Fig. 5-D and F). Such occurrence could be responsible, for instance, for the decrease in WS observed for this group after 6 months of storage in water (table 1). Since WS is calculated as a function of specimens’ mass obtained after the whole period of storage in water and the mass after the second cycle of desiccation (m_2 - m_3), greater loss of mass during 6 months of water storage may have ended up decreasing the m_2 values of these specimens and, in consequence, the values of WS for neat and solvated versions of R5, stored for this long-term period.

Differences between acetone and ethanol properties (solubility parameters, vapor pressures and bowling point) lead us to expect that the presence of these solvents in model adhesives could make them to exhibit different WS, SL and nanoleakage patterns. However, this expectation was not confirmed. We speculate that maybe the solvent concentration employed in this study would not be sufficient to determine significant differences among solvents. In relation to that, it must be said that the solvent concentration used in the current was based on that purposed by Yiu et al [4], wherein they determined the lowest concentration that can be practically reached when the same model adhesives, containing these solvents, are air-blown for prolonged time.

In accordance with previous studies, the present results also demonstrated that neat resins formulated with higher concentrations of hydrophilic functional groups (R5) absorb more water and permit higher amount of moieties release than do the least hydrophilic adhesive (R2) [13,14,22]. Accordingly, adhesive bonds made with such hydrophilic materials would be likely more permeable to water and other molecules [27]. In virtue of that, great efforts have been done to try bonding hydrophobic monomers to dentin [2,28,29]. Although this goal may be closer to be reached, dilution of adhesive formulations in organic solvent would keep being necessary due to the high viscosity of hydrophobic comonomers. Moreover, some organic solvents such as ethanol are responsible for keeping the dentin matrix dehydrated and relatively expanded to permit the infiltration of hydrophobic monomers [2]. For one reason or other, the presence of residual solvent trapped into adhesives (less or more hydrophilic) seems not to be possibly avoided. Thus, future studies may keep trying to understand the role of the residual solvent in the durability of adhesives and bonded interfaces composed by these materials.

CONCLUSIONS

Within the limits of the present study, the following conclusions can be drawn:

1. WS, SL and permeability of model methacrylate-based adhesives are more pronounced on those more hydrophilic blends;
2. Solvation of adhesive formulations determines increased WS and SL, but such effect is long-lasting only on those least hydrophilic materials;
3. Solvation of very hydrophilic adhesives may be seriously damaging in long-term.

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TABLES

Table 1: Composition and Hoy's solubility parameter of the model adhesives used in the study.

				Hoy's solubility parameters (J/cm^3)$^{1/2}$			
Material		Composition	% (w/w)	δ_d	δ_p	δ_h	δ_t
Neat Resin (Polymer)	**R2**	Bis-GMA TEGDMA CQ EDMAB	70.00 28.75 0.25 1.00	15.58	12.1	8.64	21.54
	R3	Bis-GMA HEMA CQ EDMAB	70.00 28.75 0.25 1.00	15.37	13.02	9.94	22.46
	R5	Bis-GMA HEMA 2MP CQ EDMAB	40.00 28.75 30.00 0.25 1.00	15.76	14.37	10.75	23.88
Solvated Adhesive (Polymer)	**R2 + 15% E**	R2 ethanol	85.00 15.00	15.14	11.96	10.34	21.89
	R2 + 15% A	R2 acetone	85.00 15.00	15.21	9.23	9.96	18.6
	R3 + 15% E	R3 ethanol	85.00 15.00	14.96	12.74	11.45	22.74
	R3 + 15% A	R3 acetone	85.00 15.00	15.03	10.64	10.77	19.73
	R5 + 15% E	R5 ethanol	85.00 15.00	15.29	13.89	12.14	23.96
	R5 + 15% A	R5 acetone	85.00 15.00	15.55	12.23	11.65	21.34

Abbreviations: 2MP: Bis[2-(methacryloyloxy)ethyl] phosphate; Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; CQ: camphorquinone; EDMAB: ethyl N,N-dimethyl-4-aminobenzoate; HEMA: 2-hydroxyethyl methacrylate; TEGDMA: triethylene-glycol dimethacrylate; δ_d: dispersion forces; δ_p: polar forces; δ_h: hydrogen bonding forces; δ_t: total cohesive energy density

Table 2: Water sorption (µg/mm^3) of neat and solvated versions of the model adhesive resins after 7 days and 6 months of water storage.

	7 Days			6 Months		
	Neat	**Solvated - 15% ethanol**	**Solvated - 15% acetone**	**Neat**	**Solvated - 15% ethanol**	**Solvated – 15% acetone**
R2	34.1 (4.47) ^{b,C}	83.0 (5.44) ^{a,C}	76.43 (7.26) ^{a,C}	39.1 (3.00) ^{b,C}	82.0 (5.35) ^{a,C}	74.36 (6.42) ^{a,C}
R3	61.8 (4.20) ^{b,B}	103.1 (5.71) ^{a,B}	108.86 (6.57) ^{a,B}	65.2 (2.39) ^{b,B}	101.5 (0.82) ^{a,B}	99.09 (3.84) ^{a,B}
R5	160.4 (7.65) ^{b,A}	191.7 (6.81) ^{a,A}	193.53 (4.92) ^{a,A}	143.6 (8.84) ^{c,A}	155.7 (5.06) ^{bc,A}	151.90 (3.48) ^{bc,A}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in rows) and upper case letters (analysis in columns) represent statistically significant differences among groups ($p<0.05$).

Table 3: Solubility (µg/mm^3) of neat and solvated versions of the model adhesive resins after 7 days and 6 months of water storage.

	7 Days			6 Months		
	Neat	**Solvated - 15% ethanol**	**Solvated - 15% acetone**	**Neat**	**Solvated - 15% ethanol**	**Solvated – 15% acetone**
R2	- 3.5 (4.41) ^{c,B}	49.8 (3.12) ^{ab,C}	42.84 (5.67) ^{b,C}	- 1.7 (2.39) ^{c,B}	58.0 (4.08) ^{ab,B}	62.19 (6.29) ^{a,B}
R3	- 3.5 (5.62) ^{c,B}	68.4 (6.53) ^{ab,B}	78.45 (4.25) ^{a,B}	- 1.7 (4.01) ^{c,B}	53.8 (2.88) ^{b,B}	66.77 (5.24) ^{ab,B}
R5	68.1 (9.57) ^{c,A}	141.3 (5.06) ^{b,A}	146.70 (10.89) ^{b,A}	185.1 (5.06) ^{a,A}	195.5 (4.18) ^{a,A}	203.92 (5.54) ^{a,A}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in rows) and upper case letters (analysis in columns) represent statistically significant differences among groups ($p<0.05$).

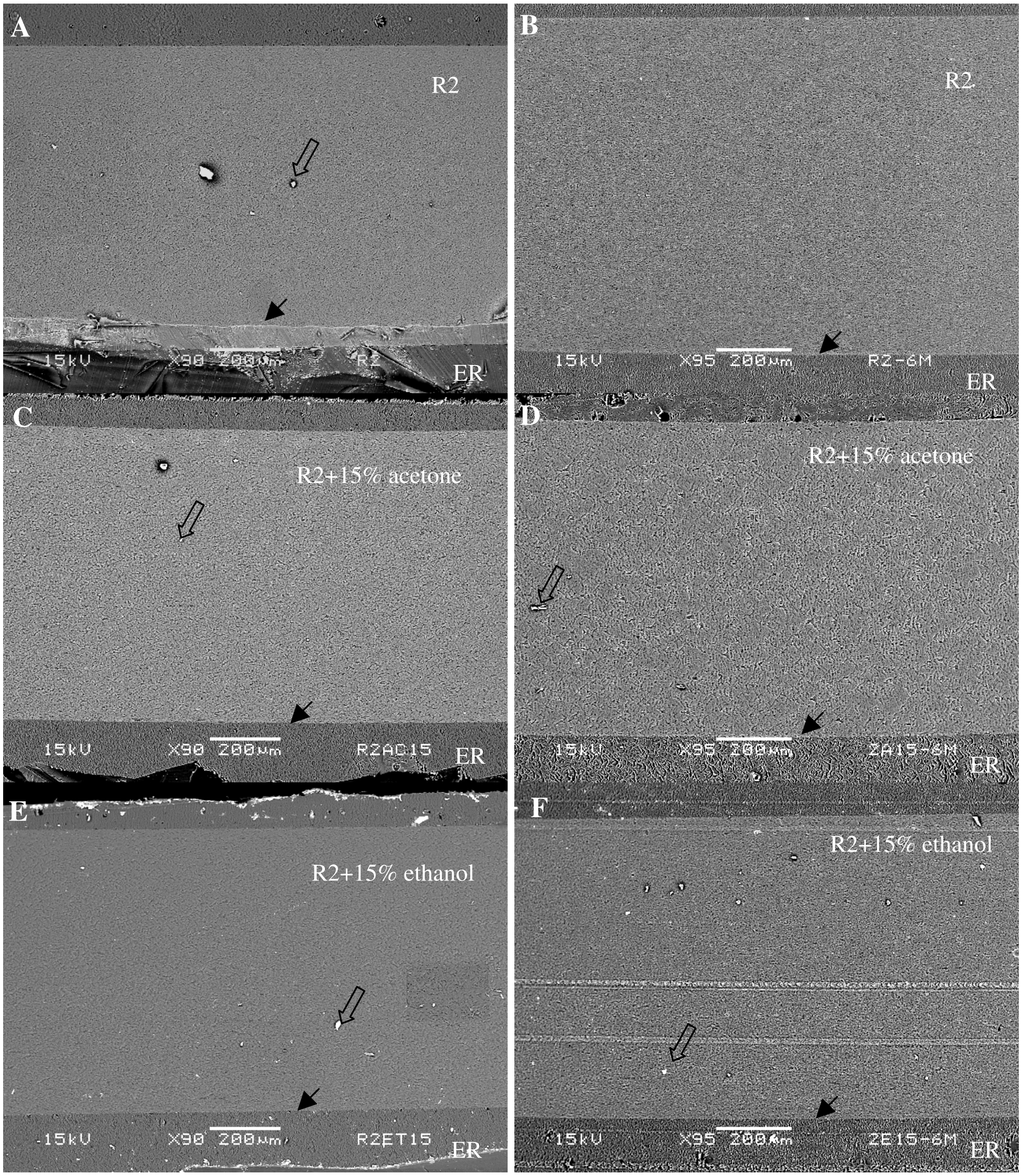

Figure 1- SEM micrographs of traced specimens of R2 embedded in epoxy resin (ER). Micrographs A, C and E are representatives of the neat and solvated versions analyzed after 7 days of water storage; while micrographs B, D and F shows the overall behavior of the neat and solvated versions infiltrated and analyzed after 6 months of storage. Almost none deposition of silver granules can be observed along the interface with epoxy resin (little arrows), or disperse over the center of the specimens (large arrows).

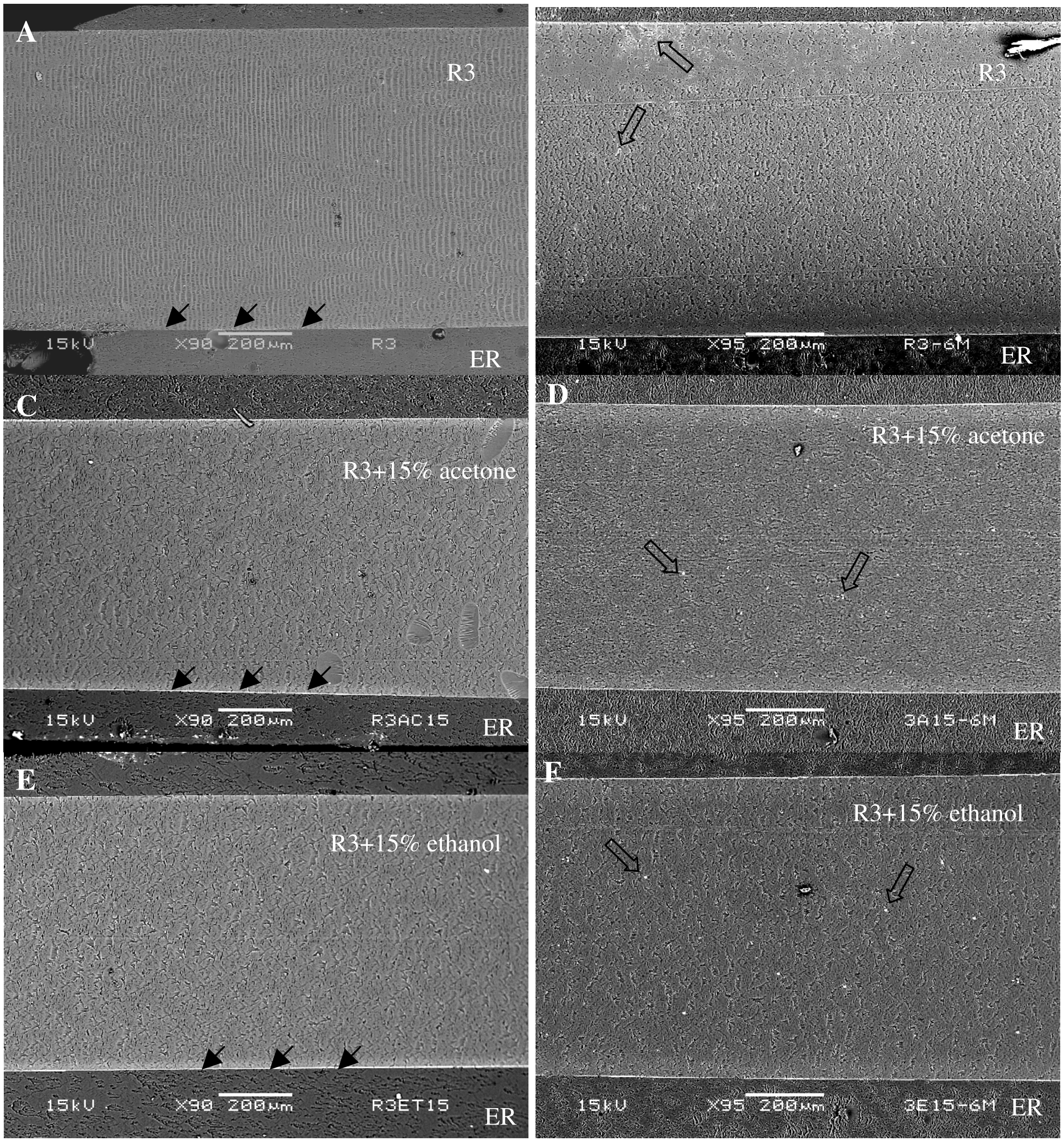

Figure 2- SEM micrographs of R3 traced specimens, embedded in epoxy resin (ER). Micrographs A, C and E are representatives of the neat and solvated versions, analyzed after 7 days of water storage; while micrographs B, D and F shows the overall behavior of the neat and solvated versions, infiltrated and analyzed after 6 months of storage. The brilliant line observed along the interface with epoxy resin (little arrows) represents silver deposition over the upper and lower superficies of the specimens. Very little deposits of silver particles can be observed disperse over the center of the specimens, after 6 months of water storage (large arrows).

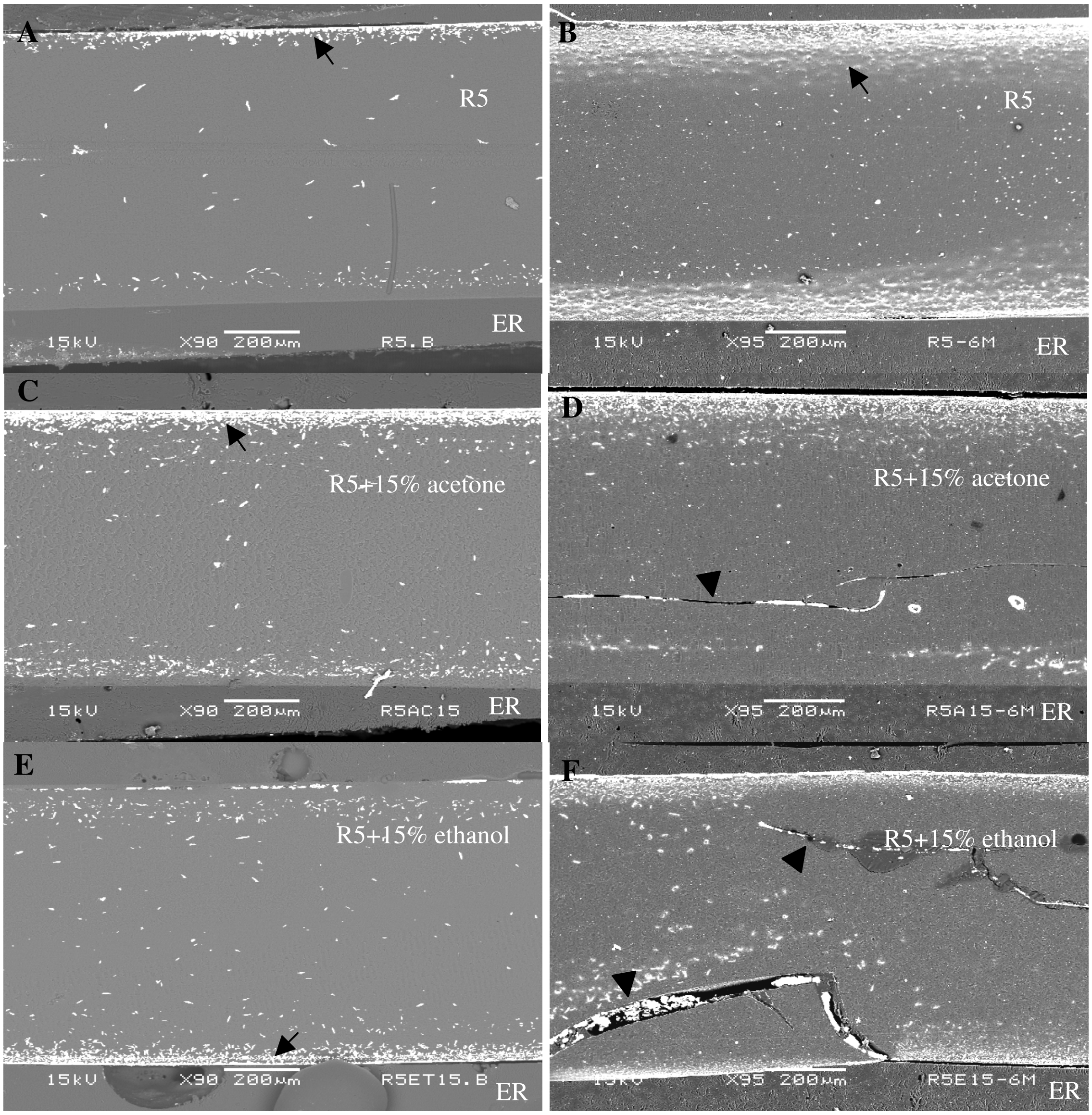

Figure 3- SEM micrographs of R5 traced specimens, embedded in epoxy resin (ER). Micrographs A, C and E are representatives of the neat and solvated versions, analyzed after 7 days of water storage; while micrographs B, D and F shows the overall behavior of the neat and solvated versions, infiltrated and analyzed after 6 months of storage. An intense silver deposition can be observed all over the specimens, regardless the solvent content or the time of evaluation. It can be observed an increase in silver deposition with solvent addition and with time of water storage. Cracks can be observed over the 6 months, solvated specimens, denoting severe damage of R5 solvated specimens when stored for a prolonged time (◄).

CAPÍTULO 3

“Permeability of dental adhesives”

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Abstract

This study evaluated the permeability of different commercial dental adhesives. Seven adhesive systems were evaluated: one three-step adhesive (*MP*); one two-step self-etching primer/adhesive (*SE*), three two-step etch-&-rinse adhesives (*SB*; *EX*; *OS*) and two one-step self-etching adhesives (*PL*; *OU*). A mixture of the primer and the bond components of SE (SE-PB) was also tested. The adhesive specimens were prepared in brass molds and immersed in ammoniac silver nitrate solution for tracer permeation. Afterwards, they were sectioned into ultra-fine cuts and prepared for scanning electron microscopy evaluation. MP and SE showed slight and superficial tracer permeation. In EX, SB and OS, permeation extended beyond the inner superficies of the specimens. SE-PB did not mixture well, and most of the tracer was restricted to the primer. In PL and OU, "water trees" was observed all over the specimens. Different materials showed distinct permeability in aqueous solution. The extent of tracer permeation varied according to materials composition, being more evident in those more hydrophilic and solvated.

Keywords: dental adhesives, hydrophilicity, solvents, nanoleakage

1 Introduction

To date, the only clinical reliable way to bond restorative materials to dental hard tissues is through the application of relatively hydrophilic dental adhesive systems that infiltrate intrinsically water-wet demineralized dentin forming the well-known hybrid layer [1]. This micro-mechanical interaction produced by infiltration and *in situ* polymerization of methacrylate monomers had so far shown to exhibit satisfactory immediate bond strength outcomes. However, in longitudinal evaluations, decreased bond strength values are found to be caused, in part, by the poor mechanical stability of the dental adhesives after relatively short periods of aging [2,3,4].

SEM and TEM micrographs of these resin-bonded restorations showed that nanopores along the hybrid and adhesive layers may increase in number and dimension even after short periods (i.e days to few months) in contact with water and/or oral fluids [5,6], contributing to reduce the sealing ability of adhesive polymers [7,8]. The permeability of dental adhesives and hybrid layers has been quoted to occur due to water sorption and subsequent solubility of the resinous components in loosely polymerized adhesives, causing plasticization and posterior degradation of the polymers linkages.

Nanoleakage protocols have been used to evaluate fluids diffusion through resin-bonded interfaces [8,9,10]. This methodology implies substrate storage in silver nitrate solution, so that silver ions are carried by water through structural nanoporosities, where they precipitate, disclosing these areas under SEM and TEM assessments. The nanoleakage expression in adhesive layers has been related with adhesives' permeability. As silver infiltration is naturally diffusion dependent, factors like the time the samples have been exposed to the silver nitrate, the size of the specimens and the nature and depth of dentin have a significant effect on the occurrence/appearance of nanoleakage [11]. Moreover, nanoleakage evaluation seems to be useful to assess the permissibility of neat adhesive systems to water infiltration and diffusion. Knowing whether the great permeability observed in bonded interfaces is a cause of materials composition, problematic application technique or both would be of great value on achieving more sealed and stable interface bonds.

In the present study, the permeability of several adhesive systems indicated to be applied on dentin under different clinical protocols was morphologically evaluated, using the ammoniac silver nitrate nanoleakage protocol [7]. The null hypothesis tested was that there is no difference in permeability to silver nitrate solution among adhesives which needs more or less clinical steps to infiltrate dentin.

2 Experimental

2.1 Materials and 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 system (Scotchbond Multi-Purpose - MP); one two-step self-etching primer system (Clearfil SE Bond – SE), three two-step etch-and-rinse adhesive systems (Single Bond 2 – SB; Exite – EX; One-Step – OS), and two single-step self-etching adhesives (Adper Prompt – PL; 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 the bond component of Clearfil SE Bond adhesive, was also tested. Composition, batch number and manufacturers for each adhesive system are listed in Table 1.

Three disk specimens (n=3) were produced for each adhesive system and for the primer+bond mixture. The uncured adhesive (approximately 200 μL) were directly dispensed into a brass mold (5.8 mm diameter, 0.8 mm thick). For the primer+bond specimens, a drop of the primer was dispensed into the mold, left undisturbed for 20 s before solvent evaporation, and then the bonding resin was dispensed over the primer until completely fill the mold. As some of the bonding resins and also the primer solution present a certain amount of solvent and/or water in their composition, a solvent evaporation procedure was done for all materials. Thus, the liquid were blown with a three-way dental air-syringe over a 30-sec period. A glass cover slip was placed on the top of the resin to exclude atmospheric oxygen and photo-activation was performed using a quartz-tungsten-halogen light source, operating at 650 mmW/cm^2, for 40 s (Elipar TriLight, ESPE, Germany). After removal from the mold, the bottom of the disks was further photo-cured for another 40 s. Any uncured resin remaining over disks surface was cleaned off with absorbent paper. After that, the disks were pre-dried in a sealed desiccator containing fresh silica gel (at 37 ºC), over a three-day period. This time was used to allow complete polymerization of the specimens and also evaporation of residual solvent enclosed into the materials [12].

2.2 Nanoleakage tracing and Scanning Electron Microscopy evaluation

After the drying process, specimens were immersed in a 50% ammoniacal silver nitrate solution according to the diamine silver impregnation protocol reported by Tay et al. [7], except for the time specimens were maintained immersed in the tracer solution. In a previous study [12], it was identified that some less hydrophilic adhesives took up to 48 hours to reach water sorption equilibrium. As silver ions are carried into polymerized adhesives by water, in a time-dependent diffusion process, this time of immersion was used for all adhesives tested. Therefore, specimens were placed in the silver nitrate solution in total darkness for 48 hours, to allow silver saturation of the specimens. After that, they were rinsed in distilled water, and immersed in a photodeveloping solution for 8 hours, under a fluorescent light, so silver ions could be reduced into metallic silver particles. The silver impregnated specimens were then embedded in epoxy resin for support. The prepared blocks were cut by the center of the specimens in order to expose its most inner surface. Polishing of the exposed surfaces was obtained using a glass knife attached to an ultra microtome. Doing so, washing of the reduced silver granules by humidity contact due to aqueous polishing was avoided. Several cuts were done over the exposed surface of the specimens until an adequate polishing was obtained. The prepared surface was carbon coated and analyzed by a scanning electron microscope (JEOL-5600 LV, Tokyo, Japan) under backscattered electrons at 90 kV. After this first evaluation, specimens returned more two times to the ultra microtome, for exposing other regions of specimens that were equally prepared to be observed by SEM. In this way, three different evaluations were performed for each specimen.

3 Results

Figures 1 to 8 depict the most characteristics 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 materials evaluated. The amount of silver deposition varied from little within the interface with the embedded epoxy resin, to severe through the entire thickness of the specimen.

Bonding resins of SE and MP (Figs. 1 and 2, respectively) showed a little silver permeation along the interface with the embedded epoxy resin. None infiltration was observed extending to the center of the specimens.

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

SB presented two distinct types of silver deposition: a granular deposition, consisting of isolated and aggregated silver granules, distributed along the interface with epoxy resin and extending to the center of the specimens; and another observed over the center of the specimens, forming elongated thin structures. In high magnifications, elongated structures seem thin fissures incompletely filled with silver (fig. 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 extends for few micrometers into the center. None deposition could be seen in the center of the specimen (fig. 5).

OS presented an intense silver permeation distributed along the margin of the specimen and also protruding to its center as isolated granules. The reticular pattern of deposition could be observed in all superficies evaluated, protruding through almost the complete specimen thickness as “water trees” like images. A curve interface with embedded epoxy resin was shown (fig. 6).

LP presented an intense silver deposition over the entire specimen. Such deposition occurred predominantly in elongated thin structures, similarly to that ones observed in SB specimens. Cracks and irregular margins were also observed (fig. 7).

In OU micrographs were predominant the granular pattern of deposition, which extended intensely over the entire specimen. Permeation was more concentrated along the interface with epoxy resin. The reticular pattern of silver deposition was also present, but smaller and more rarely observed than in OS (fig. 8).

4 Discussion

Since the introduction of the water-wet bonding technique [13] as an imperative procedure to bond resin composites to intrinsically wet acid-etched dentin, the adhesives development has been guided in order to become technically less sensitive and simpler for application. To make adhesives able to demineralize, infiltrate and bond the acid-etched dentin in minimal steps, hydrophilic monomers and organic solvents has been added in adhesives formulation. In virtue of that, it is not surprising that the most simplified systems tested in this study (PL and OU), the so-called “all-in-one” adhesives, exhibited higher amount of silver deposits than the adhesives SB, EX and OS, which represent the two-step “etch-and-rinse” adhesives. Conversely, the bonding agent of the systems, SE and MP, which are composed of more hydrophobic comonomers (i.e. Bis-GMA) exhibited significant lower deposition of silver, restricted only to their surfaces. Therefore, the anticipated hypothesis that there is no difference in permeability among the tested adhesives must be rejected.

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 water diffusion process. Thus, factors related to the increased water sorption in these adhesive systems may also explain greater silver permeation and deposition. Water sorption into polymer networks are 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 [14,15]; and network topology, which is related to the density of the polymer network [14,16,17]. Thus, in thesis, 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”, the unbound water is filling free volume and it is not expected to cause any dimensional changes of the polymer [18]; while the “interaction theory” defends that “bound” water diffusion tends to disrupt the interchain hydrogen bonding, inducing swelling and thus additional opening of interchain spaces [19,20]. Thus, as the percentage of relatively hydrophilic monomers (i.e. HEMA, BPDM, PENTA) increase in the adhesive blend, more sites for hydrogen bonding become available for “bound” water diffusion. Moreover, short length carbon-chains of hydrophilic moieties create softer polymer backbones, making easy the additional opening of free space by swelling. Therefore, a greater amount of water will be able not only to diffuse, but also to find space to accumulate inside the polymerized adhesive [21]. This explanation justifies more intense silver deposition and also the inner penetration of ions in materials that are more hydrophilic.

Apart from methacrylate monomers, primers and simplified adhesives also contain water and/or organic solvents. It has been observed that the addition of volatile solvents to adhesives formulations implies greater water sorption to the polymerized resin (Malacarne-Zanon et al., submitted for publication), what is in agreement with results obtained in this study. In fact, the extent of silver deposition into SB, EX and OS specimens increased with the amount of solvent present in adhesive’s composition, i.e. 25-35%wt, < 20%wt and 40-70%wt, respectively (Table 1). Although the solvent evaporation had been performed by air-blowing, it is likely that residual solvent may remain entrapped, especially in high hydrophilic resin blends [22,23,24]. If so, residual volatile solvents diluted in the liquid adhesive may have prevented the approximation between reactive pendant species, making the polymer cross-linking reaction more difficult [25]. Thus, instead of achieving optimal macromolecular packing density, polymer backbone may have their free space augmented in a level directly related to the amount of organic solvent present during polymerization.

The effect of solvent presence in adhesive composition was more marked in OS, the system with the highest concentration of solvent (acetone). Beyond the granular pattern of silver deposition, resultant from the silver precipitation into free spaces, a considerable amount of a reticular, water trees images were also observed in OS micrographs. In a recent work, Nunes et al. [26] reported that an acetone-solvate adhesive shows an intense molecule agitation/flux during its polymerization. Such agitation was pointed out as being a result of acetone evaporation in virtue of increased temperature generated by the polymerization reaction. Due to its high vapor pressure (200 mmHg at 25 ^{o}C) and low boiling point (56°C), acetone has greater capability to volatilize than ethanol, water or ethanol-water mixtures. Thus, it is possible that the reticular silver deposition mostly seen in OS specimens had been produced by silver permeation through the spaces left by acetone volatilization.

A great silver deposition, accompanied with several cracks, was observed in LP micrographs. The higher amount of hydrophilic monomers in LP, in relation to the other tested materials, can be responsible for such a faster and larger uptake of silver [12,22], that ended up in permanent damage of the polymer structure. Moreover, the increased concentration of water in LP, in conjunction with incompatibilities between co-initiators and the hydrophilic phase, could have rendered less monomer conversion, determining the formation of a loosely compact polymer prone to faster water/silver uptake [28,29,30].

Apart the differences in the amount of silver deposition, there were also differences in the pattern and the location of silver deposition in the tested samples. It is worthy to notice that all adhesives evaluated depicted silver permeation only or mostly along the interface with epoxy resin, i.e. in the outermost surface of the specimens, even though these were produced confined in a mold and covered with a glass slide in order to exclude oxygen surface contamination [31,32,33]. Thus, different location of silver deposition might be only explained by the non-homogeneity of polymerization in thick adhesive specimens [26], due to phase separation of very different elements [34]. With 0.8 mm thick, it is reliable to consider our specimens thick. Volatile solvents and low molecular weight hydrophilic monomers might have concentrated near the adhesive surface, causing inferior monomer polymerization in this area [25,26]. Consequently, differences in the quality of polymerization through the specimen determined the spatial anisotropy of the cured polymer, and, at last, the spatial distribution of silver particles.

Strong evidence of phase separation was specially observed in SE-PB specimens. Although care was taken to obey manufacturer's instructions during application, micrographs depicted two very distinct phases over the specimens. One poorly and another greatly infiltrated by silver particles. Such great difference forces us to speculate that primer and bond liquids do not mix. Chemical incompatibilities between these two liquids can 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 [34]. The poor miscibility between the primer and the adhesive can therefore determine the maintenance of two different phases, slightly attached by very hydrophilic and weak linkages.

The present results showed that a great amount of silver ions was able to diffuse through simplified, more hydrophilic adhesives, even though they were polymerized over an inert, water-free substrate, i.e. a teflon mold. Additionally, it was observed an intense silver diffusion through the primer of a multi-step adhesive system. Thus, despite being clinically more stable [35], 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 [36]. Based on these results, sealed bonds were only predictable if using less hydrophilic materials, like SE and MP, bonding resins of two-step self-etching primer system and three-step etch-and-rinse system. In this way, future efforts should be done to clinically bond hydrophobic materials to dental tissues.

5 Conclusion

Within the limits of the present study, the following conclusions can be drawn:

1. Simplified, more hydrophilic adhesives permits more fluids diffusion than do less hydrophilic adhesives, indicated to be applied under multiple steps;

2. Silver diffusion through one-step etch-and-rinse adhesives is related to the amount of solvent present in their composition;
3. The primer solution and the bonding resin of multiple step systems may not mix well.

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Tables

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 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 Bis-GMA catalysts	30 – 40 60 – 70 N/E	3M ESPE Dental Products, St. Paul, MN,USA
Single Bond 2 (SB)	Bis-GMA HEMA Copolymer of acrylic and itaconic acids Glycerol 1,3-dimethacrylate Diurethane dimethacrylate Silane treated silica Ethyl alcohol Water	10 – 20 5 – 15 5 – 10 5 – 10 1 – 5 10 – 20 25 – 35 < 5	3M/ESPE Dental Products, St. Paul, MN,USA
Excite (EX)	Phosphonic acid acrylate HEMA Mixture of dimethacrylates Alcohol silicon dioxide initiators and stabilizers	< 11 < 15 < 53 < 20 N/E N/E	Ivoclar Vivadent AG, Schaan, Liechtenstein
One-Step Plus (OS)	HEMA BPDM, Bis-GMA Acetone Dental Glass	10 – 40 10 – 40 40 – 70 1 - 10	Bisco, Inc. Schaumburg, IL, USA
Adper Prompt (PL)	Part A: Di-HEMA phosphate Bis-GMA Ethyl 4-Dimethyl aminobenzoate DL-CQ Part B: HEMA water	75 – 90 10 – 15 < 2 1 – 1.5 17 - 28 70 – 80	3M/ESPE Dental Products, St. Paul, MN,USA
One-Up Bond F Plus (OU)	Bonding agent A: MAC-10 metacryloyloxyalkyl acid phosphate MMA Bisphenol A polyethoxy methacrylate Bonding agent B: HEMA MMA Fluoroaluminosilicate glass filler Borate catalyst water	10 – 30 30 – 60 5 – 20 20 – 40 30 – 60 10 – 30 15 – 30 < 5 5 - 20	Tokuyama Dental Corp., Tokyo, Japan

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: methacryloyloxydecamethlene malonic acid; CQ: camphorquinone; N/E: not disclosed by manufacturers.

***Basic composition based on the Material Safety Data Sheet research.**

Figures

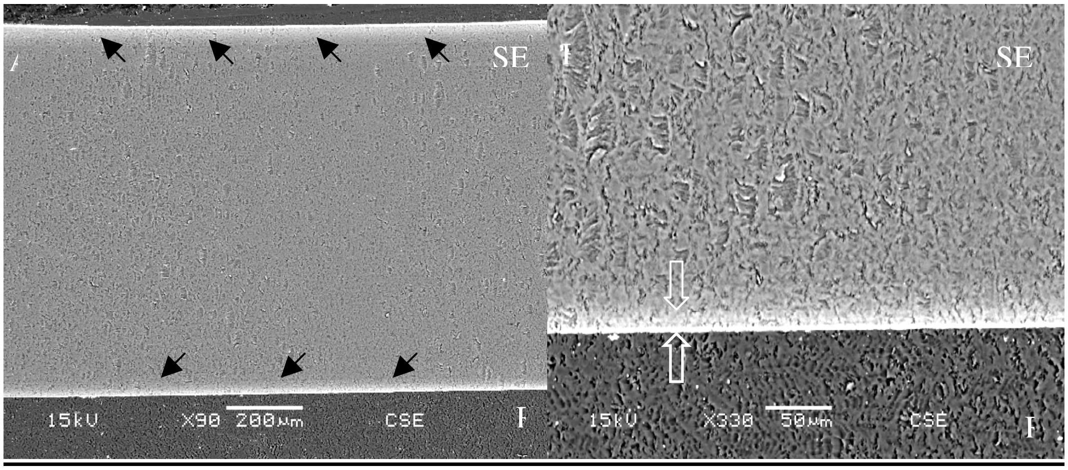

Fig. 1 SEM micrographs of traced specimens of Clearfil SE Bond (SE), embedded in epoxy resin (R), shows that silver permeation occurred mostly along adhesive-resin interface (A - arrows), with just a narrow extension into the center of the specimen (B).

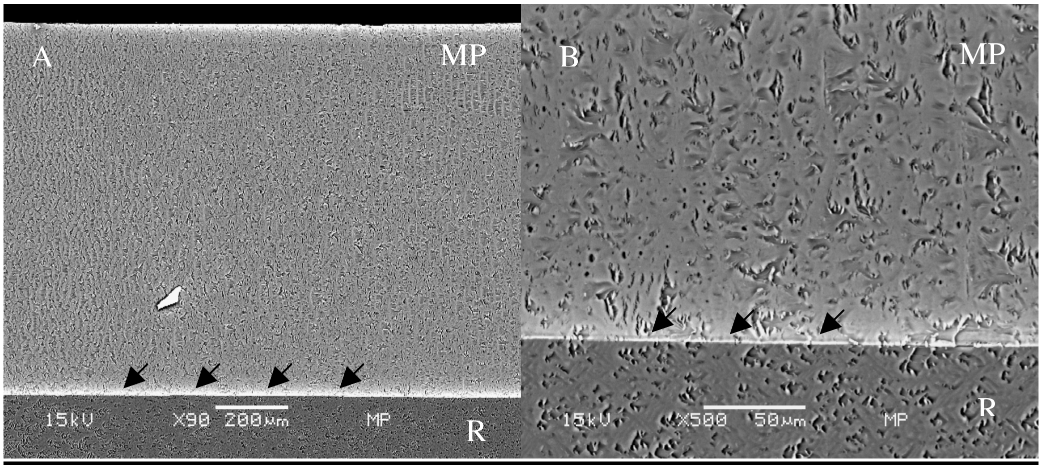

Fig. 2 SEM micrographs of infiltrated specimens of the bonding resin of Scotchbond Multi-Purpose System (MP). Even in a high-magnification SEM (B), only a slight infiltration (arrows) can be observed along the interface with epoxy resin (R).

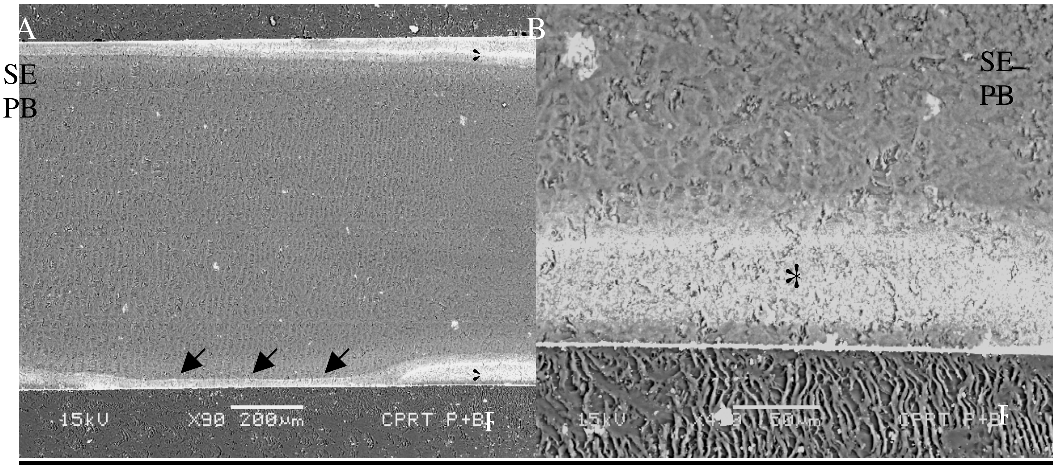

Fig. 3 SEM micrographs of traced Clearfil SE primer+bond mixture specimens (SE-PB) denote that these two components did not mixed well, since two different phases clearly separated can be seeing: one very permeated by silver (*), and another showing silver deposits mostly restricted to the interface between epoxy resin (R) and adhesive (arrows).

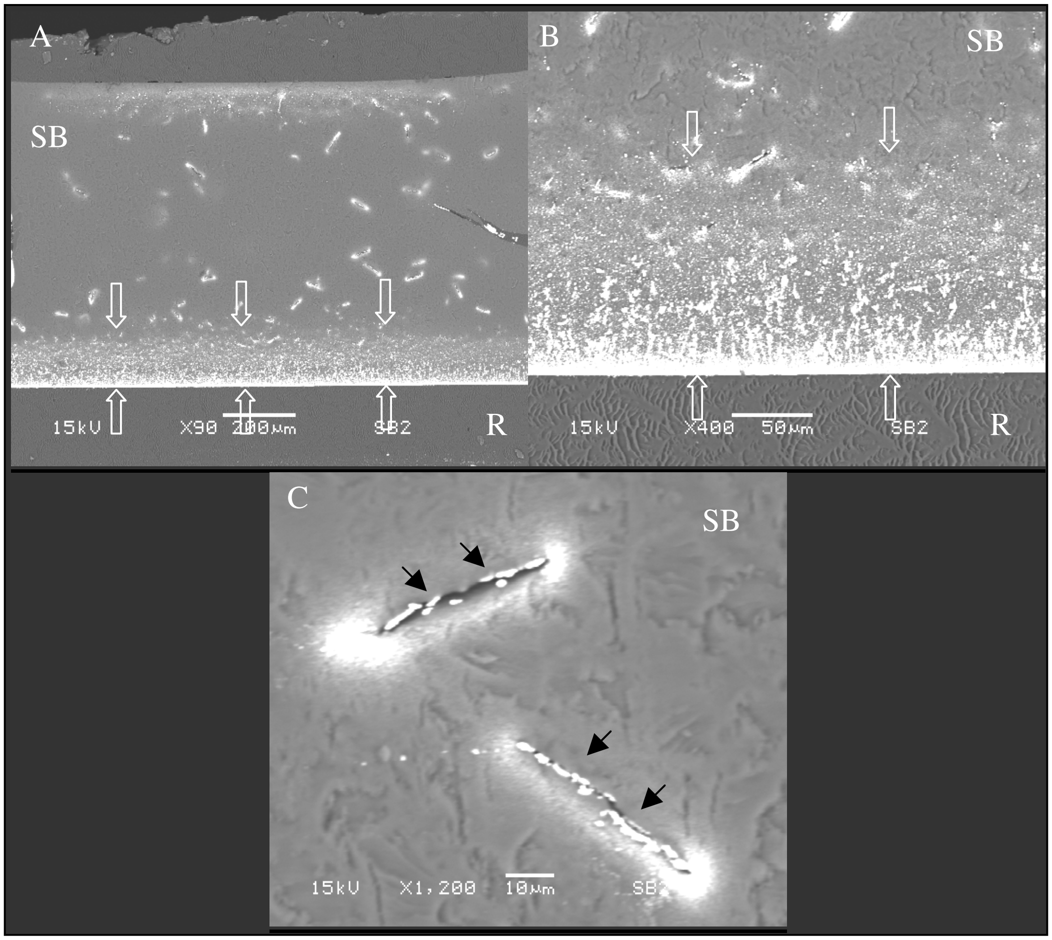

Fig. 4 SEM micrographs of infiltrated Single Bond 2 specimens (SB). In a low-magnification image (A), silver permeation over the whole inner superficies of the specimen can be observed. Two patterns of infiltration was identified: a very dense deposition of small granules (large arrows - A and B) along the interface with epoxy resin (R), and extending into the center; and a particular concentration distributed over the center of the specimens, forming elongated thin structures (arrows – A, B and C).

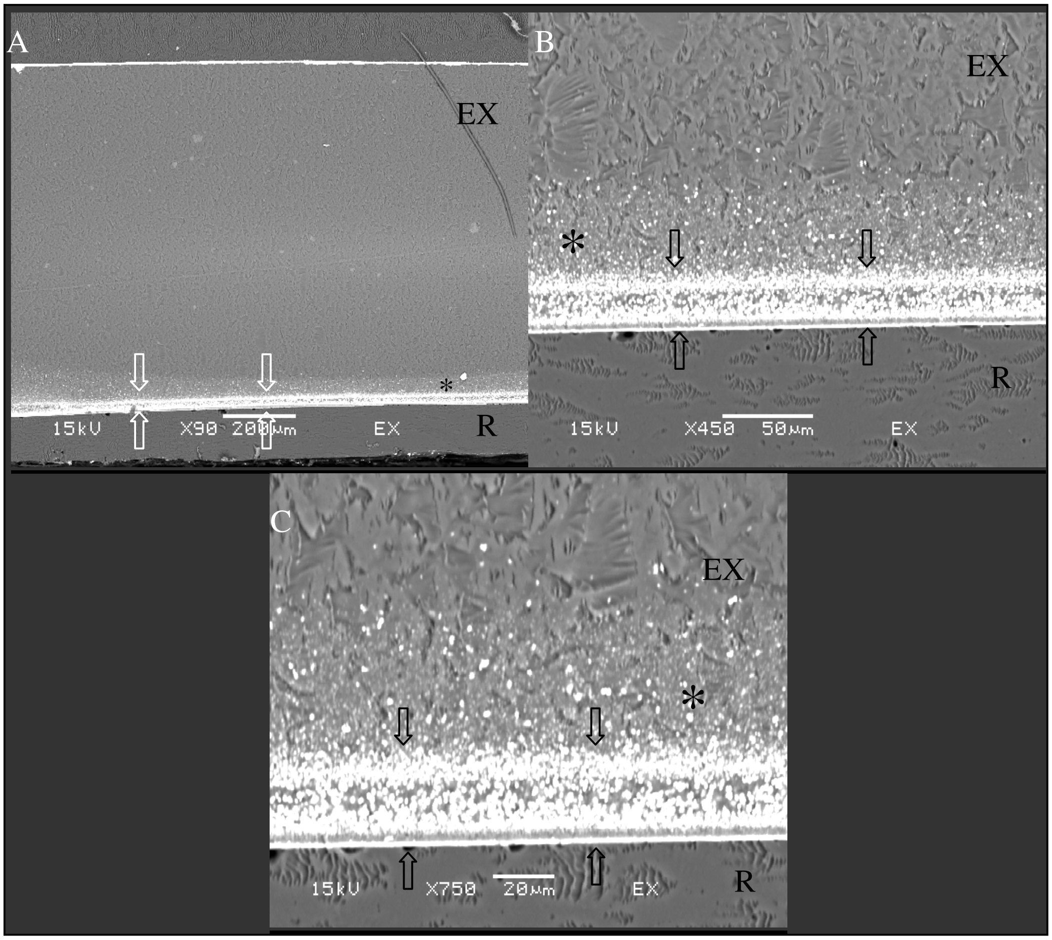

Fig. 5 SEM micrographs of infiltrated specimens of Excite (EX). A dense granular pattern of permeation (large arrows) can be observed along the interface with epoxy resin (R). Extending from this deposition into the center of the specimen, a more sparse permeation can be observed (*).

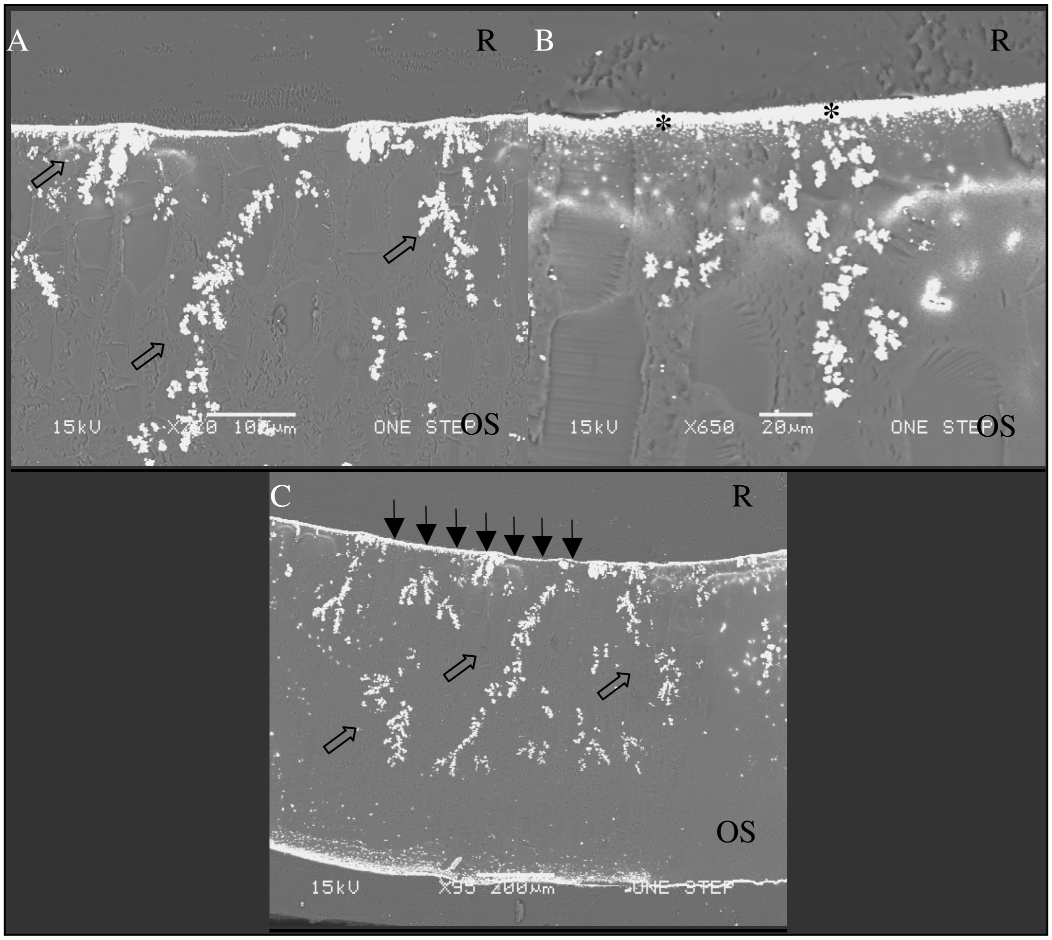

Fig. 6 SEM micrographs of infiltrated specimens of One-Step (OS). An intense silver permeation can be observed both in the superficies of the specimen and extending into the center (C). Along the superficies, the granular pattern of deposition is presented (* - B). A great number of water trees (large arrows – A and C) can be observed extending through almost the entire thickness of the specimen. The curl superficies (black arrows - C) represents the distortion occurred with the whole specimen, in function of solvent evaporation during the pre-drying period.

R - epoxy resin

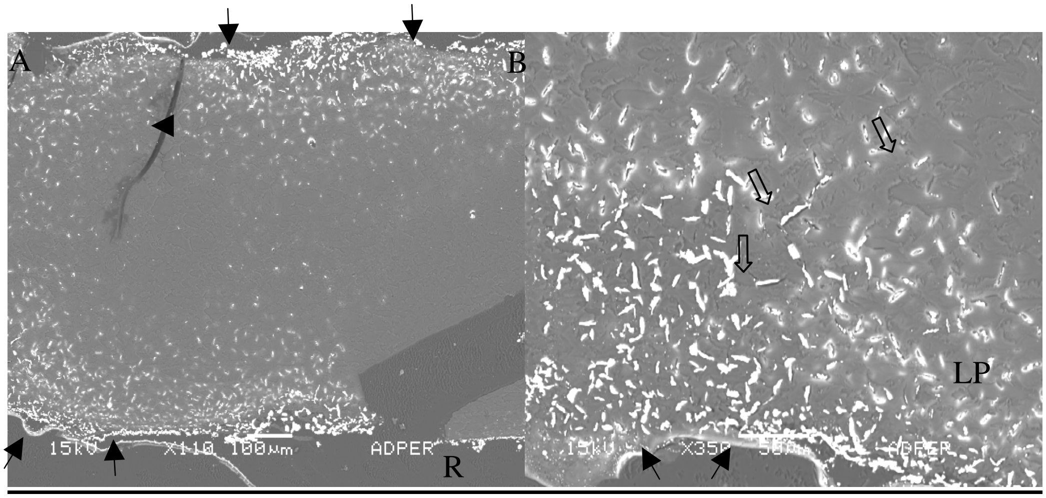

Fig. 7 SEM micrographs of infiltrated specimens of Prompt-L Pop (LP). An intense silver deposition can be observed over the entire specimen (A). Such deposition occurred predominantly in elongated thin structures (large arrows – B), similarly to that ones observed in SB specimens (fig. 4). Irregular margins represents the distortion happened to the specimen during storage in the tracer solution (arrows – A and B). In A, a crack is observed emerging from the superficies into the center direction (◀).

(R – epoxy resin)

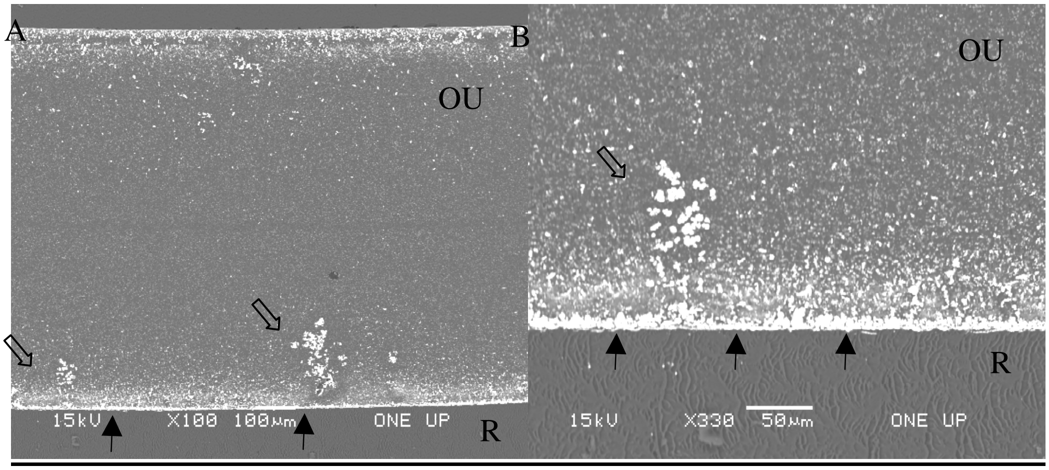

Fig. 8 SEM micrographs of infiltrated specimens of One-Up bond F (OU). An intense granular deposition can be observed over the entire specimen (A). Permeation was more concentrated along the interface with epoxy resin (R – arrows in A and B). Water trees were more rarely observed (large arrows – A and B).

CONSIDERAÇÕES GERAIS

Empregando-se as técnicas atuais de adesão à estrutura dental, os solventes presentes na composição dos sistemas adesivos assumem importância fundamental. Eles respondem pela fluidez do adesivo, pelo deslocamento da água presente na estrutura dentinária úmida (Van Landuyt et al., 2007) e também pela manutenção das fibrilas de colágeno da dentina condicionada em estado expandido (Pashley et al., 2001), garantindo, assim, adequada infiltração dos monômeros resinosos na intimidade do tecido dentinário exposto. No entanto, os indicativos de que solvente residual poderia interferir com a adequada polimerização do adesivo (Paul et al., 1999; Miyazaki et al., 2003), e, em última análise, com a sua integridade estrutural em curto e longo prazo (Jacobsen & Söderholm, 1998), estimularam a realização deste estudo.

A partir dos dados obtidos, foi observado que a presença de solvente na formulação dos adesivos, em geral, determina aumento no trânsito de fluidos através dos polímeros formados. Esse aumento, quando presente, mostrou-se dependente da concentração (5% X 15%), mas não do tipo de solvente presente (etanol X acetona). Assim, foi reafirmada a necessidade de esforços adicionais na tentativa de que maior quantidade possível de solvente seja removido do adesivo previamente à sua fotoativação. Tal condição não se faz necessária a fim de aumentar o grau de conversão dos monômeros adesivos em polímeros, como sugerido anteriormente (Paul et al., 1999; Miyazaki et al., 2003). Os resultados do primeiro estudo mostraram que a presença de etanol determina aumento do grau de conversão dos adesivos avaliados, especialmente os menos hidrófilos, R1 e R2. No entanto, esse aumento no grau de conversão ocorreu paralelamente ao aumento na permeabilidade dos materiais avaliados, o que, em última análise, determinaria acentuada degradação das propriedades físicas e químicas das estruturas poliméricas após seu contato com a água. A água atua não só na degradação química das ligações poliméricas (Göpferich, 1996), como também é capaz de reduzir as propriedades mecânicas do polímero por plastificação das suas cadeias à medida que as permeia (Yiu et al., 2004).

Nossos achados também confirmaram observações já relatadas por outros estudos, ou seja, que polímeros com maior densidade de sítios hidrófilos absorvem mais água e se solubilizam mais, permitindo maior fluxo de substâncias entre suas cadeias (Ito et al., 2005;

Malacarne et al., 2006; Yiu et al., 2006). Numa análise vertical, podemos observar aumento da permeabilidade (sorção, solubilidade e nanoinfiltração) dos adesivos conforme seus parâmetros de solubilidade aumentam. O papel do caráter hidrófilo na permeação de fluidos através dos polímeros adesivos pareceu desempenhar, inclusive, papel mais determinante que a presença do solvente. Dois achados estimulam tal especulação: os valores de sorção e solubilidade estatisticamente iguais encontrados para as diferentes versões do adesivo R1 (solvatados e sem solvente); e a semelhança nos valores encontrados para as versões do adesivo R5, armazenadas por 6 meses. As composições mais hidrófobas de R1 se mantiveram praticamente impermeáveis mesmo após sua solvatação (R1=R1 5% etanol=R1 15% etanol), ao passo que formulações muito hidrófilas se mostraram permeáveis o bastante para permitir exposição considerável de suas estruturas aos efeitos degradantes da água mesmo quando avaliadas sem solvente (R5=R5 5% etanol= R5 15% etanol). Diante disso, parece imperativo o direcionamento de esforços no sentido de se conseguir aderir clinicamente monômeros hidrófobos à estrutura dental a fim de garantir maior longevidade às interfaces de união.

São inegáveis os benefícios agregados quando materiais experimentais de composição conhecida são estudados. Por meio desses estudos, é possível determinar o efeito que cada componente desempenha nas propriedades de um adesivo, permitindo uma previsão acerca da composição ideal, capaz de garantir seu desempenho. No entanto, o conhecimento das propriedades dos materiais disponíveis para uso clínico centra o ponto de partida para o desenvolvimento de novos materiais. Assim, um terceiro estudo foi proposto com o objetivo de avaliar a permeabilidade em adesivos comerciais. Foram avaliados sete sistemas adesivos, representantes das diferentes classes de materiais indicados para aplicação à estrutura dental por meio de maior ou menor número de etapas clínicas. É sabido que, quanto mais "simplificado" o adesivo, maior a concentração de monômeros hidrófilos e solventes em sua composição, para permitir que ele infiltre as estruturas dentais em menor número possível de etapas (Carvalho et al., 2004). Por outro lado, os sistemas adesivos de três passos, indicados para aplicação em substrato condicionado por ácidos, e os autocondicionantes de dois passos, possuem um componente menos hidrófilo para aplicação sobre um *primer* basicamente hidrófilo. A presença de um componente menos hidrófilo tem sido apontada como fundamental para garantir resultados mais satisfatórios em avaliações de longo prazo das interfaces de união (De Munck et al., 2005). Assim, os materiais avaliados neste estudo foram ranqueados de acordo com sua hidrofilia, tomando-se os componentes menos hidrófilos dos sistemas de três passos e autocondicionantes de dois passos, como os mais hidrófobos; seguidos de adesivos simplificados que empregam condicionamento ácido prévio, e, por fim, adesivos ditos "todos-em-um", que contém grande concentração de monômeros hidrófilos ácidos em sua composição. Os resultados deste estudo também mostraram maior permeabilidade dos sistemas adesivos mais hidrófilos, contendo altas concentrações de monômeros ácidos e solventes orgânicos. A permeabilidade nesses materiais simplificados foi tão alta quanto a observada nas versões do adesivo experimental mais hidrófilo (R5). Permeabilidade também elevada foi verificada para os adesivos "simplificados", de condicionamento ácido prévio. Por outro lado, os "*bonds*", componentes menos hidrófilos, mostraram-se pouco permeáveis confirmando o esperado. No entanto, a partir da análise da permeabilidade da mistura *primer* + *bond*, como geralmente o sistema é aplicado, foi possível observar que a infiltração de prata no *bond* é claramente aumentada pela presença de miscelas do *primer* dispersas em sua estrutura. Foi verificado, adicionalmente, não haver mistura entre os dois componentes citados, de forma que o *bond* pudesse reforçar o *primer*, ao incluir nele monômeros mais hidrófobos. Contrariamente, é mais plausível admitir um prejuízo do *bond ao* misturá-lo com o *primer.* Assim, é sugerido que a durabilidade das interfaces de união continua baseada na estabilidade de componentes demasiadamente hidrófilos, que se comportam como o elo fraco desta interface, mesmo quando sistemas de múltiplos passos são empregados.

CONCLUSÕES

Com base nos resultados obtidos a partir dos estudos apresentados, é possível concluir que:

1. Adesivos mais hidrófilos apresentam maiores valores de sorção de água e de solubilidade, independente do tempo de armazenamento ou da condição de solvatação, sendo portanto mais permeáveis;
2. A presença de até 15% de solventes orgânicos na formulação de adesivos aumenta o grau de conversão dos monômeros em polímeros;
3. Remanescentes de solvente orgânico na formulação de adesivos hidrófilos durante sua polimerização aumenta a permeabilidade dos polímeros formados;
4. O tipo de solvente orgânico presente na formulação adesiva, etanol ou acetona, não determina diferenças de permeabilidade;
5. Adesivos comerciais de composição mais hidrófila, indicados para serem aplicados por meio de maior número de etapas clínicas, apresentam-se mais permeáveis;
6. Adesivos mais hidrófilos, contendo maior concentração de solventes, se degradam mais ao longo do tempo, apresentando maiores valores de solubilidade e sinais morfológicos de degradação física após 6 meses de armazenamento.

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